Characterization of Graphene-Epoxy Grout for Infill Material in Pipeline Repair

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Keywords: infill materials; graphene nanoplatelets; graphene-epoxy grout

Abstract. The mechanical properties of the grouts are the main factor to their potential application as infill materials in structural repair. In this research, the graphene nanoplatelets particles were added to existing commercial epoxy resin grout at the amount of 0.2% and 0.5% of weight fraction to characterize the mechanical properties of the modified epoxy grout. A control sample is used as a guide and the results will be compared with the data of control sample. Compressive tests, tensile tests, flexural tests and lap shear tests were conducted to study the effect of graphene nanoplatelets on neat epoxy grout. By comparing the strength, graphene has significantly increased the strength of grout in flexural but lower strength in compression and tension. Graphene enhances more in flexural as its orientation is parallel to the axis and perpendicular to the loading. Experimental tests results also indicate that graphene-epoxy grouts have significantly increased the modulus of elasticity in compression and flexural. The enhancements in these properties are observed to be directly proportional to the weight fraction of reinforcement materials.

Introduction

Pipelines system is known as the safest and the most efficient way to transport oil and gases over a long distance. However, a disruption in transportation of resources can happen. This piping system will fail in a number of ways and experience various types of defect that associate with either internal or external corrosion of the pipe wall. The defect pipeline needs to be repaired with the right composite material to ensure long continuous service. One of the main challenges in pipeline system is to improve the current pipeline repair technology. There are several repair component/system that exists nowadays, which involving both metallic and composite materials according to guidelines from AEA Technology Consulting [1]. Infill material is one of the composite materials that use in repairing the damaged pipes. The characterization of mechanical and thermal properties of commercially available epoxy grouts as infill material has been studied in [2]. It indicated that three out of five grouts have the potential to be used as an infill grout for composite repair based on the compressive strength.

However, the performance of infill material as part of composite repair system is not proved and there is a lack of detailed information in the research about the behaviour of infill materials in the composite repair system. Thus, it is also important to know whether this infill material could act as a secondary protection to the pipeline if the wrappings fail and whether it could provide sufficient support to the repaired pipeline. The recent discovery of graphene nanoplatelets for use as nanofillers is being studied in numerous field. Graphene can play as a structured role in improving the mechanical properties of some elements [3-4]. Hence, the experimental works are proposed to investigate the behaviour and performance of infill material with graphene content as filler to improve the role of infill material that may contribute to the improvement of composite repair system.

Literature Review

Pipelines are subjected to deterioration due to several factors, including third party damage/outside force, corrosion, material and construction defects, and mechanical failure [5-6]. Corrosion is one of a major cause of failure in both onshore and offshore pipelines [7]. As the pipeline ages, the risk for the pipeline to be attacked by corrosion is high as cyclic crack resistance for use metal of oil pipelines is lower, than for the metal of the new pipe [8].In case material losses in steel pipeline whichever by corrosion or gauging, epoxy grout used as infill material or cushion to ensure a smooth bed for the composite layer. The common used of infill material is grout and "putty" which is generally made of epoxy resin. Metal or mineral fillers are used to change the properties of filler, for example, mechanical, curing and shrinkage properties [9].

Generally, there are two separate components of composite materials which are the matrix and the filler. The matrix is the component that holds the filler together to structure the mass of the material while the filler is the material that has been saturated in the matrix to offer its advantage (usually strength) to the composite. All the coating system introduces infill material as media to provide support and transfer the load from pipe to outer shell. This load is efficiently transferred to the composite by the filler. High compressive- strength filler need to be used in the system to fill the external detect area to prevent the weakened pipe wall from further yield. The grouts that having a compressive strength of more than about 40 MPa have the potential to be used in crack repairs [10]. While a high-performance grout with the compressive strength of 85 MPa is suitable to rehabilitate fatigue damaged tubular joints [11]. Thus, epoxy grouts with compressive strength within this range have the potential for composite repair of steel pipelines. Figure 1 shows an illustration of the load transfer mechanism [12].

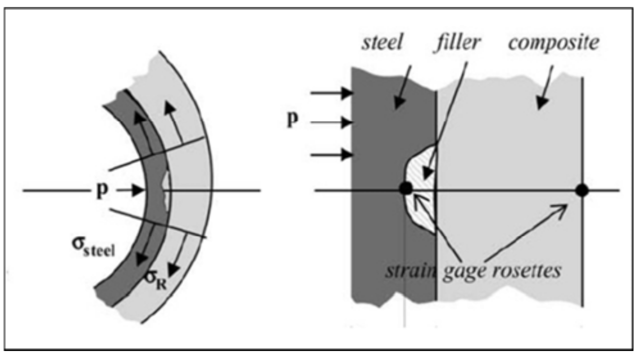

Figure 1: Load transfer mechanism

The recent discovery of graphene nanoplatelets for use as nanofillers is being studied. A number of unique properties for graphene, like their stiffness, two-dimensional geometry and also low thermal interface resistance make graphene successful filler to manufacture composite material [13,14]. Under an atomic microscope, it appeared as a single layer of carbon packed in a hexagonal (honeycomb) lattice, with a carbon-carbon distance of 0.142 nm [15]. It is suitable to be used as filler in infill material. Table 1 illustrates some of the amazing physical properties of graphene. These unique properties of graphene can be utilized for making many novel electronic devices [16].

Table 1: Physical properties of graphene

Some Basic Properties	Graphene
Young's modulus	~ 1100GPa
Fracture strength	125 GPa
Thermal conductivity	~5000 W m^{-1} K^{-1}
Mobility of charge carrier	2 x 10^5 cm^2 v^{-1} S^{-1}
Specific surface area	2630 m^2 g^{-1}

The study of graphene as coating agent was carried out by [17]. In the study, the serious global problem about rusting and another corrosion of metals were pointed out and intense efforts are ongoing to find new ways to slow or prevent it. Because of these issues, the scientists decided to evaluate graphene as a new coating. They found that graphene, whether made directly on copper or nickel or transferred onto another metal, provide protection against corrosion.

A comprehensive review and discussion on the current progress of the major challenges and future potential of graphene in the field of protective coatings can be found in [18]. In [18], the field of protective coatings is not only limited to corrosion, fouling, and mechanical wear, but also extends to adsorb toxicants, resisting frost/fire/irradiation, and killing bacteria. The combination of the unique physical structure (2D), chemical and thermal properties of graphene provides an excellent platform for these applications.

Experimental Work

Materials

The materials used in this study are grout epoxy resin and graphene nanoplatelets. A commercially available three-part pourable grout epoxy resin was selected to be used in this study. Three-part pourable grout is based on a combination of epoxy resins, hardener and specially graded aggregates (silica sand). These three materials are named as part A, B, and C with a mixing ratio of 2:1:12 by weight recommended by manufacturer's data sheet. The resin used for this experiment had a tensile strength of 14 N/mm2, a compressive strength of 100 N/mm2 and a flexural strength of 20 N/mm2. After mixing, it forms a flowable mortar which is suitable for grouting and filling.

Graphene nanoplatelets have been selected as filler that has an average thickness of approximately 0.68-3.41 nm and particle diameter is 1– 4 µm with >99.5 wt% carbon content with the appearance of black/gray powder referring to manufacturer datasheet.

Sample Preparations

The preparation of graphene-based epoxy grout by dispersing was carried out as per manufacturer's guideline. Three set of the sample with different percentage of graphene is prepared. The first set is pure grout without graphene and other two set with 0.2% and 0.5% of graphene content. Every typeof the testing required five set of the sample for every each of set. Graphene nanoplatelets were prepared through dispersion by using a high-speed mixer (Hielscher Ultrasonic) for about 30 minutes with 10% of dilution. After dispersion process, store it in the oven for 24 hours prior to use. After preparing the graphene nanoplatelets, precede the process with the mixing of graphene flake with parts A: B: C in the next following day. Figure 2 shows the process of graphene nanoplatelets dispersion.

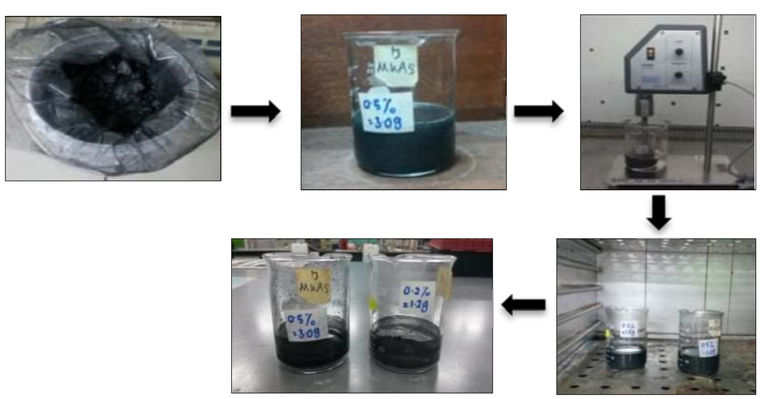

Figure 2: Dispersion process of graphene

Mix the proportion of parts A: B: C according to the ratio of 2:1:12 by weight as recommended in manufacturer's data sheet. After that, specified 0.2% weight of graphene nanoplatelets in hardener and thoroughly mixed using a high-speed electric mixer for 20-30 minute to get a homogeneous suspension. The next step was the addition of epoxy resin to the mixture and continuous mixing process until a smooth consistency paste is obtained. After the mixing of epoxy resin with graphene nanoplatelets was complete, the resin mixture was poured into specified designated moulds and cured at room temperature for one day. After that, all process was repeated with a different specified weight percentage of graphene nanoplatelets (0% and 0.5%). Figure 3 and Figure 4 shows the mixing process of graphene-based epoxy grout.

Figure 3: Mixing process of graphene flakes with hardener

Figure 4: Mixing process of graphene-based epoxy grout with part A and part C

Sample Grout A is specified as a control sample with 0% of graphene while Grout B and Grout C are the samples with 0.2% and 0.5% of graphene nanoplatelets. Each sample has same ratio proportion of epoxy resin, hardener and silica filler with 2:1:12. The detail proportions of the various elements of the grout are shown in Table 1.

Table 2: Composition of the grout sample

Grout	Component	Ingredients (Weight)			
		epoxy resin	hardener	silica filler	Graphene
A	Resin with hardener and fine filler	38.6g	19.3g	231.6g	0g
B	Resin with hardener and fine filler + 0.2% of graphene	38.6g	19.3g	231.6g	0.579g
C	Resin with hardener and fine filler + 0.5% of graphene	38.6g	19.3g	231.6g	1.448g.

Characterization

Compressive Test

All the tests were carried out using a 25 kN universal testing machine (Instron). The test was performed in accordance with ASTM: D695. Each specimen has been loaded at a cross speed of 1.3 mm/min at room temperature until failure. The typical blocks dimension for five specimens used in this testing is 12.7 mm x 12.7 mm x 50.8 mm for each specimen. All the specimens were also equipped with strain gauges to measure the longitudinal strains and axial strains. The compressive strength results were obtained by using:

$$C.S = \frac{P}{b.\ d} \tag{1}$$

Where: C.S= compressive strength (N/mm2), P= maximum load (N), b= width of specimen (mm), d= thickness of specimen (mm)

Tensile Test

Tensile tests were performed in accordance with ASTM: D638, using five specimens with dimensions of 13.0 mm x 3.2 mm. Specimens were pulled apart to failure at a crosshead speed of 5.0 mm/min and carried out at room temperature. Tensile strength and tensile modulus were achieved using the tensile curves. The area under the tensile curves determined as the material toughness. Typical stress-strain curves for each grout will be defined under tensile loading.

Flexural Test

This test method covers the determination of the flexural properties of graphene-based epoxy grout. It was performed in accordance to the ASTM D790. These tests were performed at a constant cross speed of 1.365 mm/min, at room temperature, using an appropriate device for the flexural test. Prismatic specimen block will be used in this testing. The typical blocks dimension for five specimens in this testing is 127 mm x 12.7 mm x 3.2 mm for each of specimen. For a test sample, the bending strength (σ_f) and modulus (E_B) are obtained according to equations 2 and 3, respectively.

$$\sigma_f = \frac{3.\ P.\ L}{2.\ b.\ d^2} \tag{2}$$

$$E_B = \frac{m.\ L^3}{4.\ b.\ d^3} \tag{3}$$

Where: σ_f= flexural strength (N/mm2), P= load at a given point on the load-deflection curve (N), L= support span (mm), b= width of beam tested (mm), d = depth of beam tested (mm), m = the slope of the tangent

Lap Shear Test

ASTM D1002 determines the shear strength of adhesives for bonding metals. The test specimens pulled at specifies loading rate of 1.3 mm/min (0.05 in/min). The applied force must be applied through the centerline of the specimen. The tests specimens a place in the grips of testing machine to secure the ends of the specimens align. Two specimens, each 25.4 x 100 mm (w x l) are bonded together with an adhesive so that the overlap is sufficient to provide failure in the adhesive, and not on the substrate. Typical overlaps are 12.7 mm (l_o), 25.4 mm (w) and 1.6mm for adhesive thickness. The lap shear strength results were obtained by using Equation 4:

Joint strength = lap shear strength

$$\tau \text{ joint} = \frac{F\ max}{lo\ .\ w} \tag{4}$$

Where: F *max* = force (N), w = specimen width (mm), l = specimen length (mm), l_o = length of the adhesive film (mm)

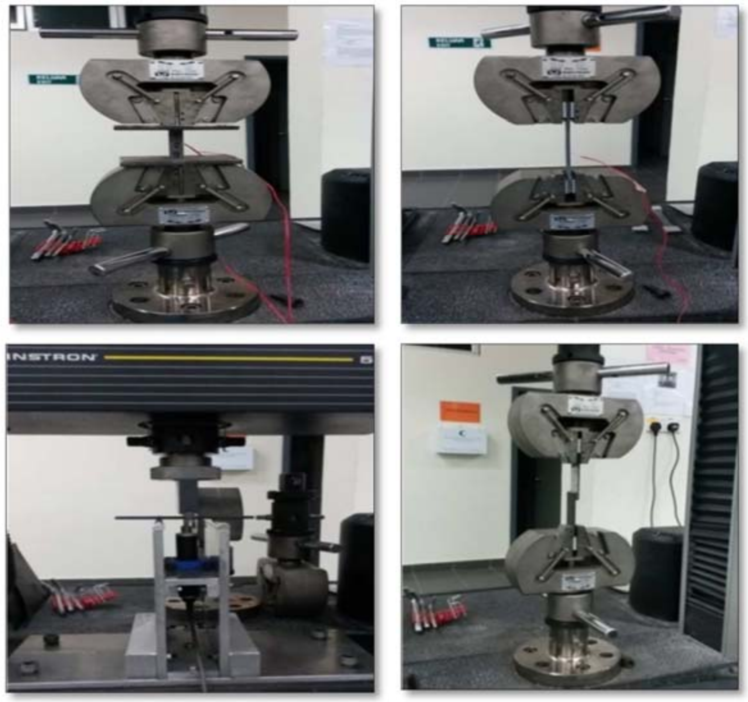

Figure 5: Universal testing machine (Instron).

Results and Discussion

Compressive Properties

Table 3 shows the summary of compressive properties of the neat epoxy grouts and graphene-based epoxy grout. From the table, Grout A exhibited the highest compressive strength of 78.62 MPa compare to Grout B and Grout C with 56.0 MPa and 53.04 MPa respectively. The lowest strength is found in Grout C. Although the strength of Grout A is higher, but the highest compressive modulus is obtained from Grout B and Grout C with a value of about 12.94 GPa and 13.08 GPa compared to Grout A with only 9.99 GPa.

Table 3: Summary of the compressive properties

Grout	Compressive	
	Strength (MPa)	Modulus (GPa)
A	78.62 ± 21.25	9.99 ± 1.89
B	56.0 ± 11.29	12.94 ± 0.62
C	53.04 ± 13.57	13.08 ± 1.01

The compression stress-strain curves of epoxy resin with 0%, 0.2%, and 0.5% graphene are shown in Figure 6. As illustrated in the graph, the three tested grout shows elastic behavior response at initial stage up to the yielding point and show declination of stress after the yield point. Furthermore, from the stress-strain curves of the compressive test, it illustrates that the graphene-epoxy grout shows increasing in young modulus as the curve in elastic region is stiffer compared to neat epoxy grout. As the young modulus increase, the grout with graphene content break at lower strain fracture than neat epoxy grout at certain stress.

Figure 7 demonstrates the failure patterns of the tested grouts under compression loading. Initial cracks were observed at top and bottom part of the sample where the maximum stress occurred.

Through observation, there is no significant lateral expansion on the grout samples. The noticeable deformation surface failure is obviously shown on tested grout. The sample displayed split inclined crack at the top of the sample.

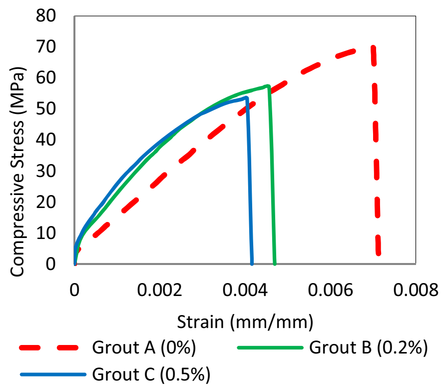

Figure 6: Typical stress-strain curves for compressive stress

(a) (b) (c)

Figure 7: Failure patterns of grouts under compression (a) Grout A (b) Grout B and (c) Grout C

Tensile Properties

Table 4 provides a summary of the tensile properties. It can be seen from the table that the tensile strength of the investigated grouts are in the range between 11 to 19 MPa respectively and tensile modulus for tested grouts are approximately 17 GPa. From the test results, the highest tensile strength was obtained from grout A with 0% of graphene content with 19.11 MPa.

Table 4: Summary of the tensile properties

Grout	Tensile	
	Strength (MPa)	Modulus (GPa)
A	19.11 ± 1.82	17.35 ± 4.19
B	12.54 ± 2.50	17.17 ± 5.53
C	11.58 ± 4.14	17.21 ± 6.02

The comparison of the typical stress-strain behaviour of sample grout under tensile loading is shown in Figure 8. All grout display lower ductility under tension compared to compression. From the graph, it can be seen clearly that the elastic zone for the tested grout is almost identical and this indicated that the young modulus of graphene-epoxy grout is equivalent to neat epoxy grout. The graphene epoxy grout has failed at lower strain compare to neat epoxy grout. Under tensile load, all the tested grout has failed due to splitting which is perpendicular to the length. Figure 9 shows the failure pattern of the specimens under tension.

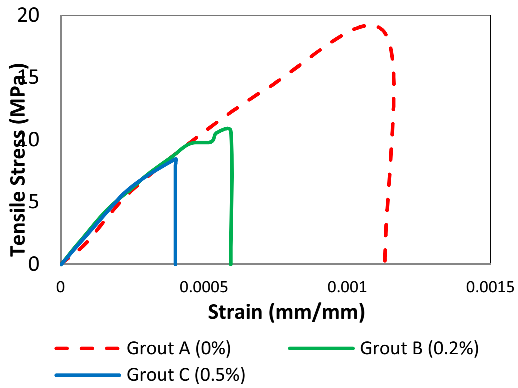

Figure 8: Typical stress-strain behavior of tensile specimens

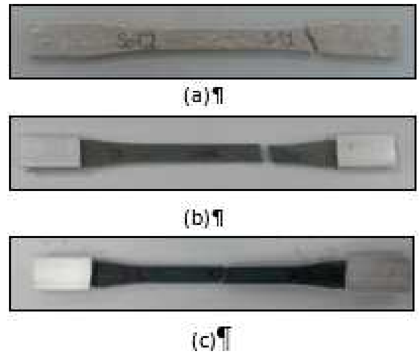

Figure 9: Failure patterns of grouts under tension (a) Grout A (b) Grout B and (c) Grout C

Flexural Properties

Table 5 presents the flexural strength values for both tested grouts. As shown in the table, graphene-based grout has the higher flexural strength compared to neat epoxy grout. Grout C with 0.5% of graphene content has the higher flexural strength with 36.07 MPa compare to grout A and grout B. Other than that, grout C also exhibited the highest stiffness compared to another two grout where the value of flexural modulus obtain was 14.54 GPa. The flexural strength and modulus of modified epoxy grout were clearly improved compared to the neat epoxy grout.

Table 5: Summary of the flexural properties

Grout	**Flexural**	
	Strength (MPa)	**Modulus (GPa)**
A	31.95 ± 6.12	11.50 ± 2.23
B	35.16 ± 1.30	13.35 ± 1.39
C	36.07 ± 2.71	14.54 ± 1.81

Figure 10 shows a typical comparison graph of the load-deflection behaviour of specimens under flexural loading. Each of sample specimens shows linear elastic load-deflection behaviour prior to failure. From load-deflection graph, it is shown that neat epoxy grout has lower load strength and also has lower deflection than graphene epoxy grout. Besides, graphene-based epoxy grout exhibited the highest load strength as well as higher deflection. Figure 11 shows the typical failure pattern of the grout specimens under flexural. All tested grouts fail in a brittle manner. The crack formations for grout A, B and C are almost vertical and perpendicular to the length of the grout specimens.

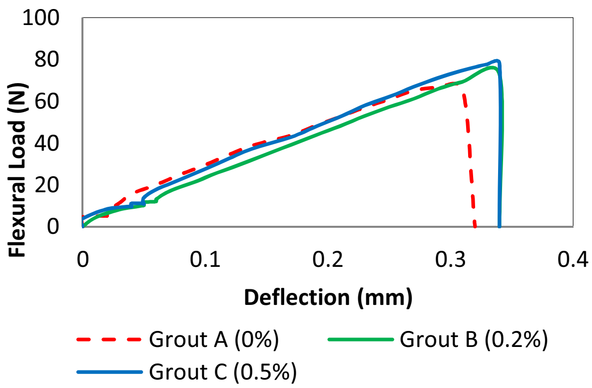

Figure 10: Typical flexural load-deflection behaviour

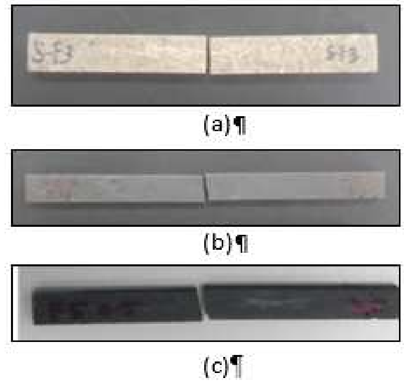

Figure 11: Failure patterns of grouts under flexural (a) Grout A (b) Grout B and (c) Grout C

Lap Shear Properties

The single lap shear joint adhesive test is to demonstrate the different behaviours of adhesives during and after a tensile loading. On the average, grout C with 0.5% of graphene content had highest shear bond strength than grout A and grout B. The bonding strength of epoxy grout increase with the presence of graphene. The shear testing result is illustrated in Figure 12. On the other hand, Figure 13 shows the loading at failure with grout C shows the highest load fail with 1261N and the lowest failure load is grout A with 518N.

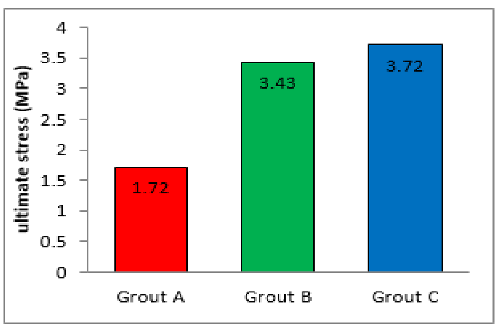

Figure 12: Ultimate stress of grout from lap shear test

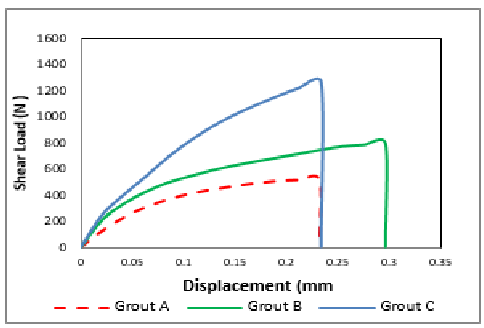

Figure 13: Load-Displacement behaviour

Figure 14 demonstrates the failure patterns of the tested grout. Under tension load all specimen grout exhibit adhesive failure behaviour. In addition, the failure has occurred at the interface of the post and core material while the adhesive remained undamaged.

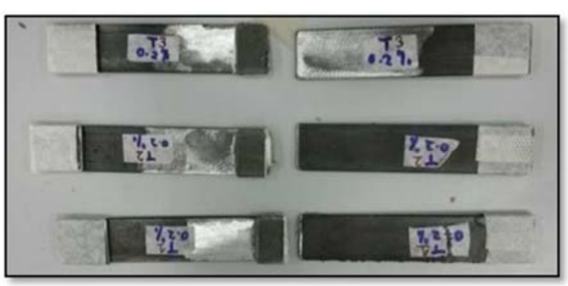

Figure 14: Failure pattern of lap shear test

Discussions

In terms of its properties, graphene certainly has the potential to increase the strength of infill material [19]. However, in this research, the mix data results have been obtained. First, the discussion will cover the performance of graphene in term of compression. From the observation, the addition of graphene content in epoxy grout has decreased the strength but yet increase the modulus of the grout. This can be explained as graphene essentially has reduced the strain of matrix in compression as the gap or void between matrixes has been filling in by graphene. However, in term of strength, it is found to be much lower that neat epoxy grout due to sudden rupture because once it fills the gap it will reduce the ductility of the matrix hence make it more brittle and lead to sudden rupture.

In tensile, there is no significant change in the modulus. However, the strength has significantly reduced. This can be explained by considering the low interaction between the graphene sheet and the matrix which has induced a very weak interface. This weak interface has prevented the load transfer from matrix to graphene filler. In tension, the bonding interaction is more importance than the bridging effects. Even though the graphene has fills the gap in the matrix but because of the bonding and interaction is very weak hence there is no change to the modulus and also a reduction in strain. At the same time, graphene may interact and interrupt the matrix. This explains why the strength in tensile is lower.

However in flexural it found that graphene has significantly increased the strength. This is because on the flexural test the load is perpendicular to the specimen sample. Theoretically, the orientation of the graphene is mostly in line with the axis and almost perpendicular to the loading. Hence, it has explained why there is an increment in the strength of matrix.

Through the lap shear testing, the results show the adhesive failure occurred where the adhesive completely losing its bond to the substrate. Adhesive failure results in one panel without adhesive and the other with the entire adhesive. The two chemicals are useless by themselves but, mixed together, form a tough and permanent adhesive. In term of lap strength, graphene was found to increase the roughness of the surface of the matrix. Hence, the mixture of grout with graphene has increased the bonding strength of particle with the material in contact. It verifies that the component will be durable throughout its service life.

Conclusions

A laboratory experiment was conducted to investigate the characteristics of existing infill material with the addition of graphene nanoplatelets. The impact of utilizing graphene as filler was assessed based on the laboratory test results. Based on the objective of this study, the following conclusions can be drawn:

1. The mechanical properties of the selected existing commercially epoxy resin have been characterized to be compared to the properties of the modified epoxy resin. The compressive strength and modulus of selected commercially epoxy and graphene-epoxy grout range from 53 to 79 MPa and 10 to 13 GPa, respectively. Furthermore, the tensile, flexural and shear strength of the grout ranges from 9 to 19, 32 to 36, and 2 to 4 MPa respectively. The tensile and flexural stiffness of the grout is found to be within the range of 17-25 and 11-15 GPa.
2. The research proved that when 0.2% and 0.5% of graphene content was added to the existing infill material, it has changed some of the mechanical properties of the material. Expansion of graphene in epoxy resin has enhanced more in flexural as compared to compressive and tensile strength which is affected by increasing in the degree of graphene presence. Other than that, graphene also has significantly improved the mechanical properties of grout specified in stiffness as its leads to increasing in young's modulus of the material. Furthermore, the bonding quality between the substrate and metal plate where it is in contact is also increased.
3. As far for the overall conclusion, kenaf fibrous concrete is a good rehabilitation or repairing materials for concrete. Kenaf fibrous concrete can improve the tensile strength bonding with

other concrete as well as compressive strength and shear strength by increasing the kenaf fibrous concrete grade.

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