EFFECTIVE DISPERSION OF GRAPHENE NANOPLATELETS IN EPOXY GROUT FOR STRUCTURAL REHABILITATION

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Thesis submitted in fulfillment of the requirements
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DEDICATION

To my beloved parent,

Mr. Kasmaon Darusman and Mdm. Laili bt Othman.

Thank you for your unconditional love and support!

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ABSTRAK

Saluran paip bawah tanah adalah cara paling selamat untuk mengangkut minyak dan gas. Pada masa kini, banyak teknik pemulihan dan kaedah pembaikan boleh didapati untuk membaiki saluran paip di darat dan luar pesisir pantai termasuk penggunaan komposit polimer diperkuat gential (*FRP)*. Sistem pembaikan komposit yang melibatkan tiga bahagian iaitu pembungkus komposit, pelekat dan bahan *infill* adalah teknik yang paling disukai untuk membaiki saluran paip yang rosak dalam industri minyak dan gas. Kekuatan bahan *infill* yang tinggi mempunyai potensi untuk meningkatkan prestasi pembaikan secara keseluruhan. Tujuan penyelidikan ini adalah untuk mengkaji keberkesanan penyebaran *graphene nanoplatelets* sebagai penguatan untuk meningkatkan prestasi bahan epoksi sebagai *infill*. Dengan menambahkan 0.01%, 0.05% dan 0.1% *graphene nanoplatelets* ke dalam epoksi, penyebaran telah dilakukan dengan menggunakan mesin *three-roll mill* di mana graphene adalah diuraikan untuk mencapai penyebaran yang sekata. Ujian sifat mekanikal telah dijalankan mengikut ASTM D638 untuk ujian tegangan dan ASTM D695 untuk ujian mampatan. Keputusan ujian tegangan dan mampatan menunjukkan peningkatan kekuatan untuk semua sampel yang diubah suai. Kekuatan tegangan tertinggi dicatatkan pada 20.89MPa untuk sampel dengan 0.1% graphena dan 82.67MPa untuk sampel ditambah 0.05% graphena untuk kekuatan mampatan. Peningkatan kekuatan yang dicatatkan adalah antara 46% hingga 88% dan 3% kepada 16% di bawah ujian tegangan dan mampatan. Oleh itu, berdasarkan penemuan kajian ini, graphene menunjukkan keupayaan untuk meningkatkan prestasi ujian tegangan dan pemampatan berbanding dengan sampel kawalan.

ABSTRACT

Underground pipeline is the safest ways to transport oil and gas. Nowadays, a lot of rehabilitation techniques and repair methods are available for onshore and offshore pipelines including the usage of Fibre-Reinforced Polymer composite. Composite repair systems involving three parts which are composite wrapper, adhesive and infill materials is most preferable techniques used for repairing damaged pipeline in oil and gas industry. High strength infill materials has the potential in improving overall repair performance. The purpose of this research is to investigate the effectiveness dispersion of graphene nanoplatelets as reinforcement to enhance the performance of epoxy grout as infill materials. By adding 0.01%, 0.05% and 0.1% of graphene nanoplatelets, the dispersion was done using a three-roll mill machine where the graphene was de-agglomerate to achieve homogenous dispersion. The mechanical properties tests were carried out in accordance to the ASTM D638 for tensile test and ASTM D695 for compressive test. The results of tensile and compression tests show increment of strength for all modified samples. The highest tensile strength was recorded at 20.89MPa for sample with 0.1% graphene and 82.67MPa for sample added 0.05% graphene for compressive strength. The strength increment was recoded range from 46% to 88% and 3% to 16% under tensile and compression test, respectively. Thus, based on the findings, graphene nanoplatelets shows the ability to improve performance for tensile and compressive properties as compared to control sample.

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LIST OF SYMBOLS

km	kilometre
m/s	Metre per second
µm	Micro metre
rpm	Rotational per minute
mm	Milli metre
%	percentage
±	Plus minus
mm/min	Milli metre per minute
$\bar{x}$	Mean
n	Total numbers
s	Standard deviation
$\sum x_i$	Summation of value
MPa	Mega pascal
GPa	Giga pascal
N/mm^2	Newton per milli metre square

LIST OF ABBREVIATIONS

MAOP	Maximum Allowable Operating Pressure
FESEM	Field Emission Scanning Electron Microscope
SOP	Standing Operating Procedure
ASME	The American Society of Mechanical Engineer
ISO	International Organization for Standardization
FRP	Fibre Reinforced Polymer
SWNT	Single-Walled Carbon Nanotube
CN	Cyanoacrylate
UTM	Universal Testing Machine
GnP	Graphene nanoplatelets
CV	Coefficient of variation
Eq.	Equation

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Structure rehabilitation techniques involving repairing or upgrading pipelines systems in civil engineering applications are techniques that commonly used in oil and gas industry. Pipeline in oil and gas industry are being used to transport products such as oil and gas across various soil environment and from offshore to onshore plant. Malaysia has its own pipeline network, the Peninsular Gas Utilization which comprising mainly of gas transmission and supply pipelines and spans over 2500km across peninsular Malaysia (Petronas Gas Berhad, 2017). Most of the pipelines that have been used for transporting products are subjected to various types of damage after long service year (Saeed et al., 2014). The factors that contribute to the pipelines damage includes corrosion, natural forces, construction defect and third parties damaged (Lim et al., 2016). Obviously, pipelines surface that exposed to the water and soil environment will have higher corrosion risk due to active chemical reaction by is surrounding environment (Bernardo et al., 2016). Most of the pipelines that have been operated for long duration that subject to damage needs repair and maintenance to ensure that it can operate smoothly and safely. This is very important for the safety and economy purpose of public and pipeline operators.

Based on previous studies, a few of articles were come out with better solutions for repairing pipeline (Lim et al., 2016; PipeAssure™, 2017). Generally, repairing methods have been developed in order to extend the safety and durability of damaged pipeline. There are two ways to repair pipeline which are conventional steel sleeve and composite repair system (Lim et al., 2016). Conventionally, pipelines are repaired by removing the entire damaged section or using steel sleeve/clamp to reinforce the damaged pipe. The conventional repair method have several disadvantages including safety issues due to hot work, bulky, have limited applications for joints or bends and subjected to corrosion risk in the future. The Clock Spring (2017) show that the composite pipe repairs are stronger than the original pipe, allowing to perform at original Maximum Allowable Operating Pressure (MAOP) and it has been endorsed by peer review and third-party testing in oil and gas industry. The advantages of composite repair system include lightweight, high strength and stiffness, and good corrosion resistance. Even though composite repair systems offer numerous advantages, several issues regarding the performance of the composite repair systems are not fully understood. These issues include conservativeness in existing design codes, effect of defect geometry, and performance and contribution of infill materials. Some of them ignoring the function of the infill materials and mostly focused on the improvement and the performance of the composite wrapping component. They assume that the epoxy grout used is only to fill the void/defect of the damaged pipeline without reinforcement on the pipeline.

1.2 PROBLEM STATEMENT

In general, a composite repair system consists of three mains part: (i) composite wrapper; (ii) adhesive; and (iii) a high compressive infill material. The composite wrapper is used to wrap at the area of repair section. An adhesive is acting as a glue that apply at every single layer of the composite sleeve. Infill materials carry important role of transferring load from pipeline to the composite wrapper and as secondary layer to carry load of the repaired pipe. However, most of previous researches ignoring the function of the infill materials and mostly focused on the improvement and the performance of the composite wrapping component. They assume the function of the epoxy grout is only to fill in the void of the damaged in the pipeline without reinforcement to strengthen the damaged pipe. Since infill is part of the repair component it should somehow contribute in strengthening the damaged section. Therefore, it is hypothesized that by using higher strength infill, it can contribute to overall repair performance.

Numerous researchers have mentioned that the nanofiller system will give the better properties improvement in epoxy grout (Tang et al., 2013; Yue et al., 2014). Since the discovery of graphene nanoplatelets, it have been widely used to improve mechanical properties graphene/epoxy grout (Tang et al., 2013). To achieve enhancement of the mechanical properties of the epoxy, there are several issues need to be addressed, for example, improvement of the dispersion of graphene in resin. This is because, the poor dispersion of the graphene inside the epoxy not only decrease the efficiency but also would cause the graphene slip on each other when force applied on the composite. The good dispersion of graphene will affect the mechanical properties and may enable the extraordinary potential for making advance materials (Yue et al., 2014).

Based on the previous studies, dispersion of nanofillers inside the epoxy resin can be very challenging for researchers (Singhi, 2015). One of the reasons is the low viscosity of resin will cause poorer dispersion of nanofiller. This is one of the reasons why this research needs to be conducted to achieve better result of dispersion. Therefore, this study aims to investigate the dispersion of the graphene nanoplatelets in epoxy grout and it is hypothesized that good dispersion will enhance the performance of the infill materials towards pipelines repair.

1.3 OBJECTIVES

The main aim of this study is to increase the performance of infill material in the composite repair system by experimental test:

1. To modify the mechanical properties of commercially available epoxy grout by adding graphene nanoplatelets via calendaring technique.
2. To study the effect of graphene nanoplatelets as reinforcement of epoxy grout towards tensile and compressive properties.
3. To determine the nature of failure of the reinforced epoxy grout sample by using Field Emission Scanning Electron Microscope (FESEM).

1.4 SCOPE OF STUDY

This study investigates the effectiveness dispersion of graphene nanoplatelets into infill materials to increase performance of the reinforced epoxy grout for repairing damaged steel pipeline. This study is not a development of new material but an attempt to increase the performance of the existing epoxy grout. The performance of the infill materials was determined by investigating the strength and stiffness through tensile and compression tests. Next, selected samples were examined by Field Emission Scanning Electron Microscope (FESEM) test to investigate the nature of failure of the reinforced epoxy grout. The percentage of reinforcement (graphene nanoplatelets) that used in this study were 0.01%, 0.05%, 0.1%.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter provides discussion on the behaviour and performance of the infill materials use for pipeline repair in oil and gas industry. Other than that, the pipeline history had been introduced in this chapter. Generally, pipeline system need to be repaired after long service time. There are various pipeline repair techniques including conventional steel sleeve/clamp and fibre-reinforced composite system. Discussion about these repair methods is included in this chapter. In addition, design codes concerning the composite repair of pipeline are reviewed. This chapter ends with the discussion of the issues on the techniques of dispersion of graphene nanoplatelets in the epoxy composite.

2.2 HISTORY OF PIPELINE

Oil pipeline industry has been developed since 1860's. The primary oil pipeline was constructed in 1862 which was basically built out of two wooden board combined to create a "V" shape for transportation of product. Development of pipeline technology is continued by utilizing steel pipeline for transporting oil and started growing due to greater need of the products from the public (Clark, 2015). Several countries have been exposed to this technology as well as Canada where it has built its first transmission pipeline in 1862 as shown in Figure 2.1. The 25km cast-iron pipe moving natural gas to its required destination and it was the longest pipeline in the world during that time. The market demand for oil and gas products increase by time due to the industry development and the oil and gas pipeline network has been expanding during 1950s. Nowadays, Canada has 11900 km of underground transmission pipeline (Hays, 2015).

Figure 2.1: Transmission pipeline transport crude oil from Edmonton,Wiscinsin, USA (Hays, 2015)

In Malaysia, early development of petroleum and natural gas occurred at the end of the 19th century. In 1910, the first oil well was drilled in Miri, Sarawak. It was started by the Royal Dutch Shell exploration and it brought Malaysia's first offshore oil field on stream in 1968. Technology development for offshore exploration and drilling in 1970 has contributed to the kick-start of oil and gas industry in Malaysia. Malaysia's crude turns out to be the most high-quality product with low sulphur content. To date, Malaysia has 3km of condensate pipelines, 1757 km of gas pipeline, 155km liquid petroleum gas pipeline, 30 km of oil pipeline. (Hays, 2015).

As the time goes by, the pipeline system will undergo deterioration and some of the pipeline system also subjected to damage after long service duration. Other than that, the structural pipeline that was hidden beneath the ground continues to be problematic on a daily basis where it could cause damages to the pipeline system. There were few incidents reported on these damages. The CBS News reported in year 2017, more than 100 gallons of oil in North Dakota has leaked from the Dakota Access pipeline system and these incidents happened in two separate occurrences in March 2017. Moreover, a flange that connects two sections of pipeline was found to be leaky at a pipeline terminal. This has caused spills about 84 gallons in Watford City on the same month. The surrounding areas of the incident were not affected at all as the oil flow was immediately cut off. In addition, another leakage has also occurred in Mercer County which was caused by failure of an above-ground valve due to a manufacturing defect (Bismarck, 2017).

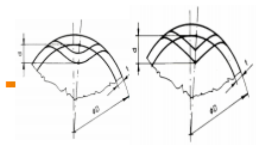
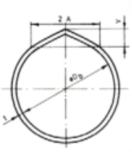
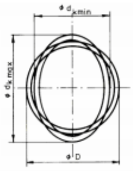
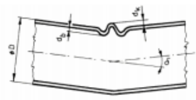
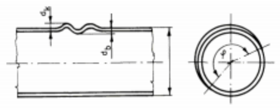
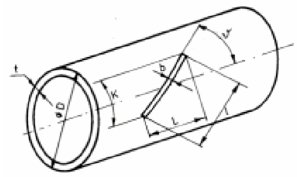
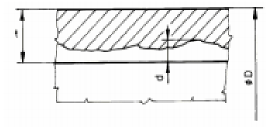
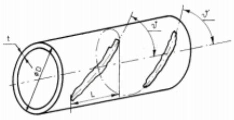
National Transportation Safety Board (2014) investigated the pipeline accident that occurred at West Virginia where the pipeline ruptured at the scattered area. This has immediately caused an ignition of high-pressure natural gas. The main safety issues that recognized from this incidents were decaying of coating of pipeline, an inadequate inspection and testing of pipeline, weak of management and lack of valve system in order to improve isolation of high-pressure pipelines (Virginia, 2012). Hence, there are various factors contributing in the defects of a pipeline that restricted the operation.

2.3 PIPELINE DEFECTS

All the physical materials in this world will undergo deterioration after long service duration. Pipeline is one of the materials that will suffer from corrosion either at its internal or external surface area. Besides that, other factors that cause damages to the pipeline are decay or environmental effects that may lead to the remedial works of a pipeline system. Pipeline damage can be classified into four types: (i) Geometrical defect; (ii) Defects resulting in metal loss; (iii) Planner discontinuities; (iv) Change in metal (El-sayed, 2017).

Table 2.1 shows the types of pipeline damage in oil and gas industry. Geometrical defects are minor changes in thickness of wall of pipeline that produces stress accumulation. Defects resulting in metal loss are damage that caused by major changes in the thickness of the wall of pipeline which could results in concentration of stress. The planner discontinuities happen when two dimensions are significantly greater than the third one. Last but not least, changing in metal will give a disadvantageous towards the material characteristics yet it does not affect any changes in the shape of the geometry of the pipe.

Table 2.1: Types of pipeline defects (Miesner, 2011)

Geometrical defects	Smaller change in wall thickness that the allowable wall thickness tolerance and result in stress accumulation and concentration.    Buckle: regular & sharp Rolling imperfection Ovality   Wrinkle Ruck
Defects resulting in metal loss	Greater change in wall thickness than the allowable wall thickness tolerance and result in stress concentration.   General location scar General corrosion
Planner discontinuities	Two dimensions are significantly greater than the third one.   Stress corrosion crack Lamination
Change in metal	Do not cause (or the change does not exceed the allowable limit) in dimensions or shape of pipe geometry but they result in disadvantageous change in the materials structure and by this way in materials characteristics.

All the types of damaged pipeline need to go through a standard operating procedure (SOP) to ensure the remedial works will abide with its safety regulations. There are two types of standard that have been developed to guide the repair works of pipeline damages which are The American Society of Mechanical Engineer (ASME) and The International Organization for Standardization (ISO). The ISO has developed ISO/TS 24817 design standard in 2006 to standardize for both steel and pipeline composite repair and it covers for petroleum, petrochemical and natural gas industries. ASME has developed the ASME PCC-2 code in 2015 that specifically covers the steel pipeline repair. As a general guide, Table 2.2 summarizes the types of defects that can be repaired using composite based on ASME PCC-2 and ISO/TS24817.

Table 2.2: The guide to generic defect types

Types of defect	**Applicability of repair system**	
	ISO	ASME
General Wall Thinning	Y	Y
Local Wall Thinning	Y	Y
Pitting	Y	Y
Gouges	R	R
Blisters	Y	Y
Laminations	Y	Y
Circumferential Cracks	Y	R
Longitudinal Cracks	R	R
Through-wall Penetration	Y	Y

Y implies generally appropriate

R implies usable but requires extra consideration

2.4 TYPES OF REPAIR FOR DEFECTIVE PIPE

2.4.1 Conventional Steel Repair

Steel pipelines are effective and it is the safest way as the underground long-distance pipe. Steel pipelines are high strength, has relatively simplicity of joint and low cost. Before this, the conventional types of pipelines repair is done by removing the entire damaged pipe and replace it with a new pipe. Other than that, welded steel patch, full-encirclement steel sleeve and steel clamp are also categorized as conventional repair system. These repair systems include joining 2 pieces of steel by bolting or welding it onto the outside surface of the damaged pipe (Lim et al., 2016). Full-encirclement steel sleeve can be divided into two types; Type A and Type B as shown in Figure 2.2. Type A sleeve act as reinforcement for damage area by welding two pieces half-circle steel sleeve longitudinally while Type B is same repair method as Type A but with additional step where the end of the sleeves are welded circumferentially to the carrier pipe. The additional step of Type B can repair the leaking defects or defects that are predicted will be leaking in the future. Besides, steel clamp repair as shown in Figure 2.3 also can be used for repairing damaged pipeline. The conventional repair method has several disadvantages including safety issues due to hot work, bulky, have limited applications for joints or bends, and subjected to corrosion risk in the future. Hence, researchers are looking for alternative solution in repairing damaged steel pipelines.

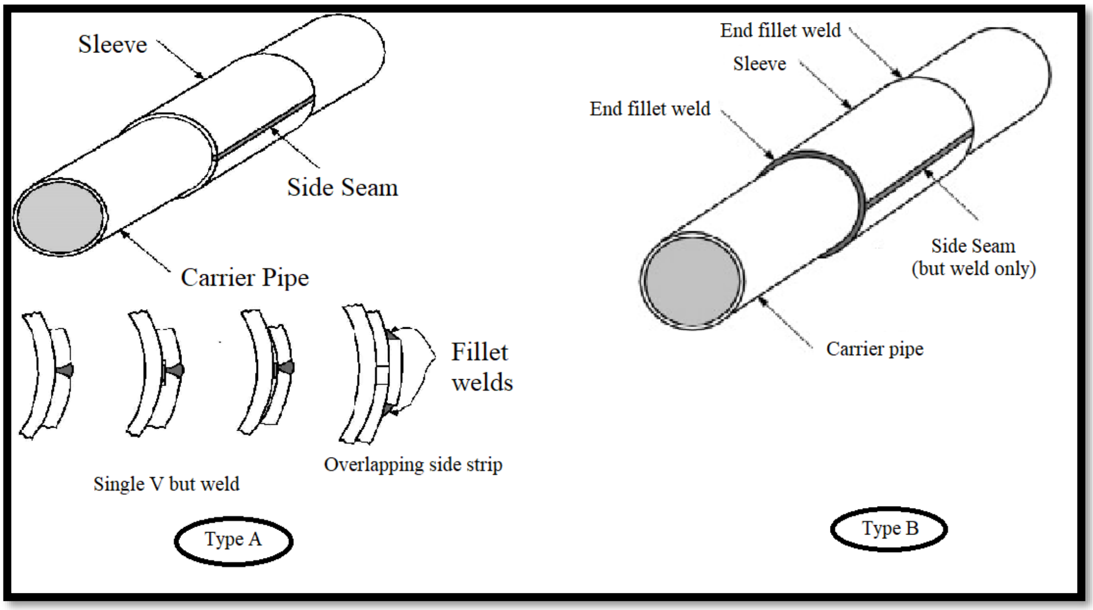


Figure 2.2: Full-encirclement steel sleeve

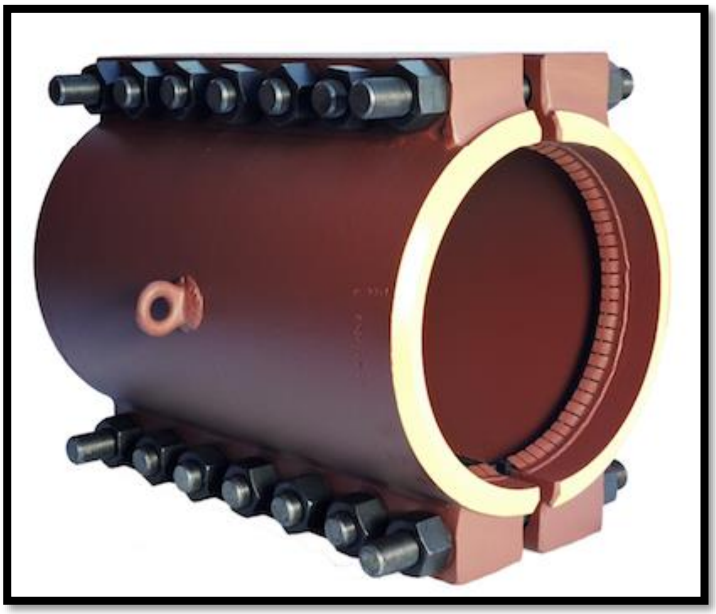


Figure 2.3: Steel clamp pipeline repair system

2.4.2 Fibre Reinforced Polymer (FRP) Composite Repair System

Composite materials have been commercially used in several industries including pipeline repair industry. This is because, composites have been accepted as a legitimate repair material based on international standards, the ASME PCC-2 and ISO/TS 24817. Furthermore, a lot of advantages of composite in repairing pipelines have been proven such as saving in terms of cost and time. An analysis done by the industry shows that the composite repair system is, on average, 24% cheaper than welded steel sleeve repairs and 73% cheaper than completely replacing the damaged section of the pipeline (Duell et al., 2008). Besides the cost, this repair system also offers benefits such as (1) reduced repair time, (2) the uninterrupted operation of the piping system during repair, and (3) safer since it eliminates the need for welding and cutting of pipeline (Duell et al., 2008).

Composites pipeline repair systems mainly have three components: (1) composite sleeve, (2) interlayer adhesive, and (3) infill material. Basically, the first step of repairing pipeline using these 3 components is using the infill materials to fill the surface of damage part of the pipeline. Then, the adhesive is used as the glue to connect between damaged pipe, infill material and composite sleeve. Finally, the repair is considered done after curing process of infill and composite sleeve. Figure 2.4 and 2.5 show the components of the composite repair system and the step for repairing damage pipeline.

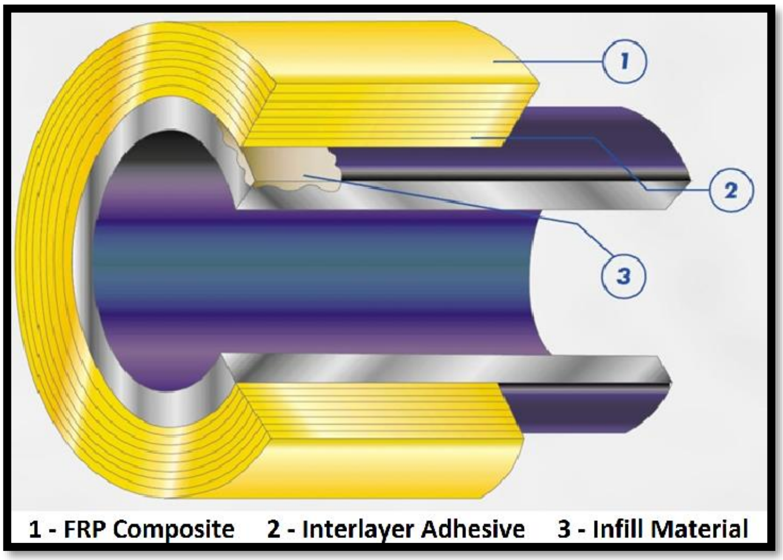


Figure 2.4: FRP composite repair system (The Clock Spring Company, 2017)

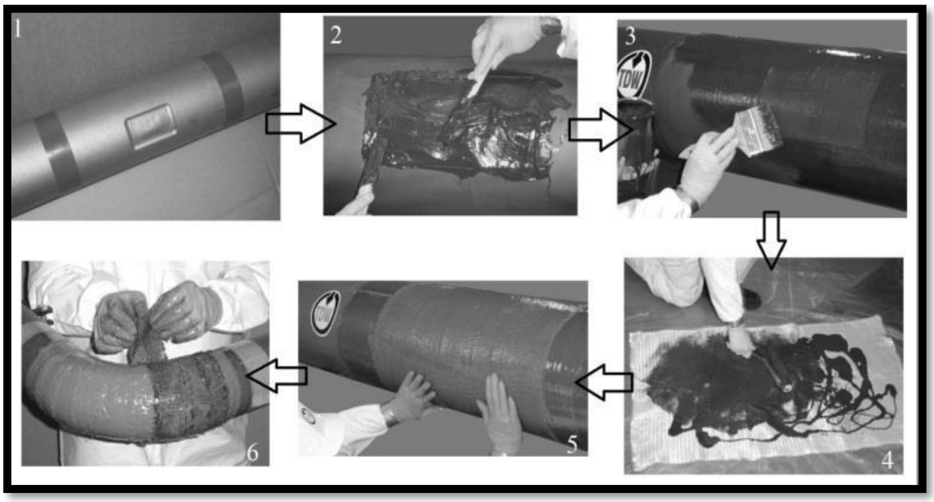


Figure 2.5: Step installing the fibre-reinforced composite wet lay-up pipeline repair

Despite the above-mentioned advantages, previous works have been ignoring the function of the infill materials and mostly focused on the improvement of the performance of the composite wrapping component. The function of the epoxy grout used for repair is commonly understands as filling the void of the damage/defect in the pipeline without contributing any strength. In recent years, a study done by a researcher indicates that infill materials can contribute to the strength of the repaired pipeline (Lim, 2017). The infill is covered by wrapping composite and compressed by internal pressure of the pipe so that the increasing in strength of infill materials will aid to carry load from the damaged section to the composites wrap of pipelines. Thus, the enhancement of the infill material needs to be improved because it has the potential to increase the contribution in the repair system.

2.5 ENHANCEMENT OF INFILL MATERIALS

The enhancement of performance of the infill materials is carried out by adding nanofillers such as graphene nanoplatelets to the epoxy grout. The function of the nanofillers as a reinforcement is to enhance the mechanical properties of the polymer. Graphene nanoplatelets is suitable to be used as reinforcement in this research due to its extraordinary physical properties (Shadlou et al., 2014). This is because graphene nanoplatelets is 200 times harder than steel and 30 times harder than diamond (Anwar et al., 2016). Even though the graphene is stronger than diamond, simply adding of graphene into the epoxy grout will be insufficient to improve the mechanical properties. In order to gain benefit from the graphene nanoplatelets, good dispersion is essential. Poor dispersion of graphene may lead to deterioration of the mechanical properties of the reinforcement in infill material. Previous researchers have developed several techniques used to achieve effective dispersion of nanoparticles in epoxy grout.

Liao et al., (2004) conducted an experiment to investigate the dispersion process of single-walled carbon nanotube (SWNT)/SC-15 epoxy resin nanocomposite. The authors found that combining solvent dilution and tip sonication is one of the method for improving nanotube dispersion and improving the mechanical properties of epoxy resin nanocomposite. Other than that, Wang et al., (2016) also conducted an experiment about the enhancement of fracture toughness, mechanical and thermal properties of graphene/epoxy and it was expected that uniform dispersion of graphene nanoplatelets in viscous epoxy grout created by three-roll mill calendaring (EXAKT, D-22851) can be achieved due to the high shear forces between the adjacent rollers. It can be seen in the Figure 2.6 that dispersion of the reinforcement. This had been shown that the dispersion of the epoxy grout impacted the improvement of strength of the infill materials. So, calendaring method is one of the effective methods to improve the mechanical properties of the epoxy grout and can be considered as suitable method to be used in this research.

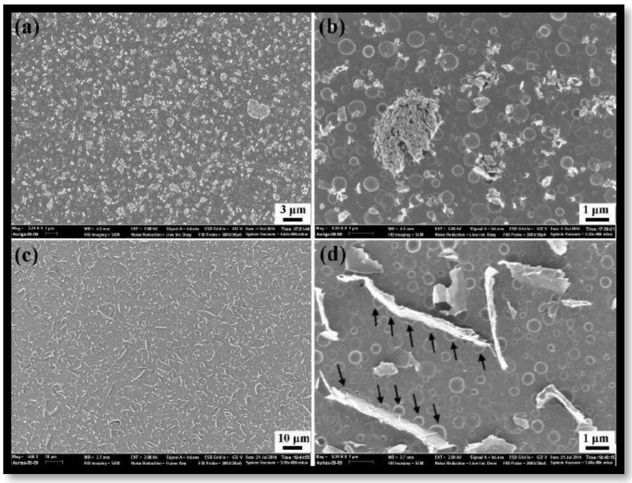


Figure 2.6: SEM images for (a) low magnification and (b) high magnification; dispersion of GnP-5 in 3 wt.% GnP-5/CTBN/epoxy composite, (c) low magnification and (d) high magnification

2.6 CONCLUSION

As a conclusion, there are a lot of the previous studies have been reviewed in improving the repair techniques for pipeline system in oil and gas industry. FRP composite repair system is the method that carries a lot of advantages to the public and industry. However, some of the components for composite repair systems still need to be improved to increase the strength and stiffness of the infill materials. This has led researcher to study about enhancing the performance of the infill materials without development of any new materials. Good dispersion of reinforcement in epoxy grout has been expected to make the infill having higher strength. Therefore, this research proposes to enhance the properties of infill materials using suitable nanofiller (graphene nanoplatelets) and dispersion method (three roll mill).

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

Two research stages have been conducted in order to achieve the research objectives. Stage 1 aims to modify the mechanical properties of commercially available epoxy grout by adding graphene nanoplatelets via calendaring technique. 50 samples were formed during the material preparation and the performance of the epoxy grout has been tested. The samples were formed into dog-bone shape and prism shape for tensile and compression test respectively. Stage 1 is very important and need to be carefully conducted to get better result. The result of Stage 1 contributes to the first objective in this study.

Stage 2 carries two objectives to be achieved. One of the objectives aims to study the effect of graphene nanoplatelets as reinforcement of epoxy grout towards tensile and compressive properties. The modified-epoxy grouts were produced by adding 0.01%, 0.05% and 0.1% of graphene nanoplatelets into commercial epoxy resin. The performance was measured by comparing the epoxy grout with and without nanofiller via mechanical properties. Upon the completion of this step, the mechanical properties of epoxy grouts were determined.

The other part of Stage 2 which contributing to the last objectives of this study was achieved using Field Emission Scanning Electron Microscope (FESEM) method. The nature failure of epoxy grout was studied after undergoes the tensile test. The failure part of the materials had been cut into the suitable sizes for scanning under the microscope. FESEM provided additional input on details of the failure surface of the specimens. This method can increase the understanding of the root of failure. The overall research methodology is illustrated in Figure 3.1.

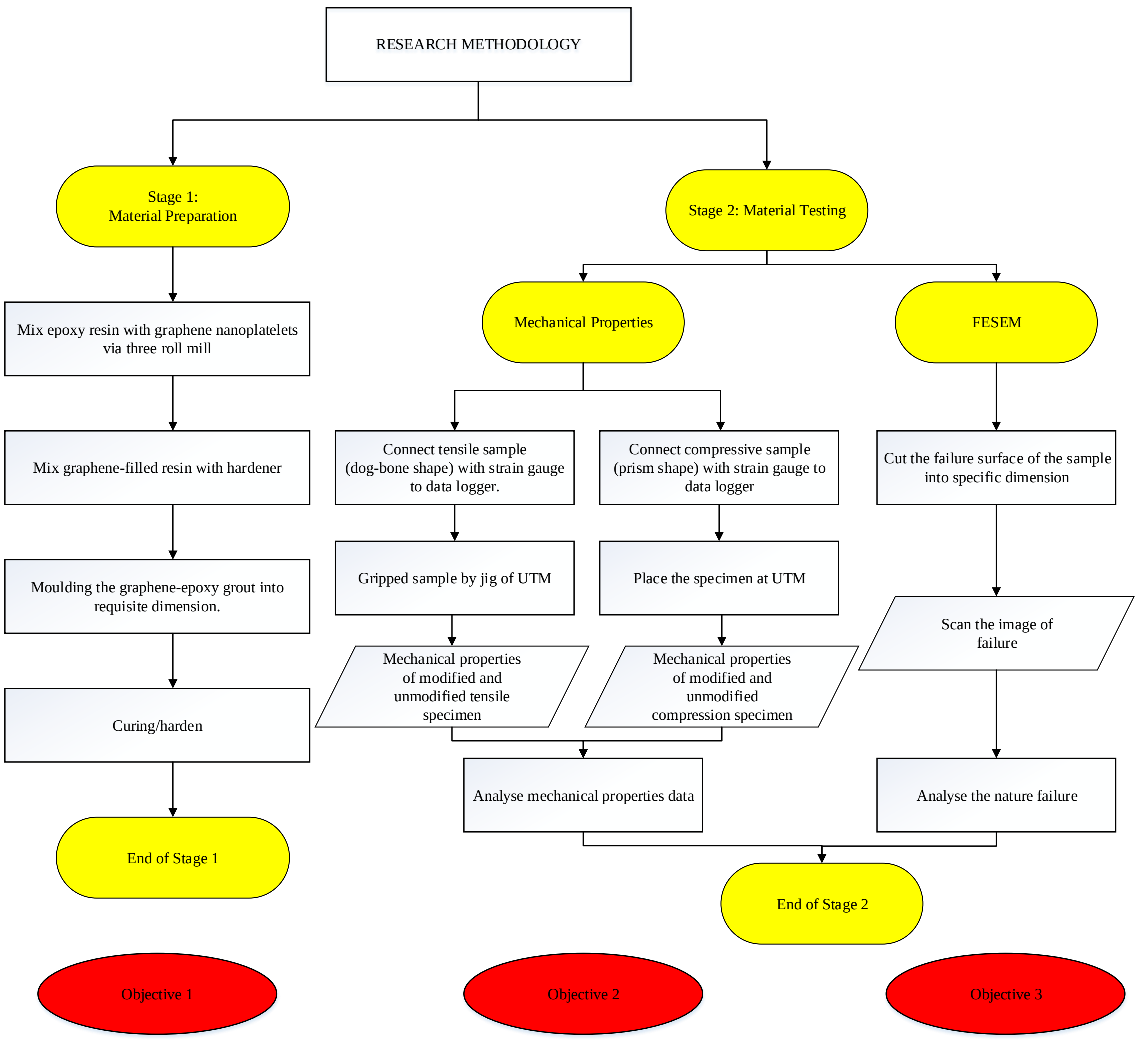


Figure 3.1: Overall flowchart of this study

3.2 STAGE 1: MATERIAL PREPARATION

The flow chart of materials preparations is shown in Figure 3.3. The first step done was the modification of neat epoxy where the epoxy grout was prepared according to the guidelines. The modification of neat epoxy starts with mixing epoxy resin and graphene nanoplatelets using planetary centrifugal mixer, the Kakuhunter SK-350TII. The graphene was added at different percentage into the epoxy resin and transfer into Kakuhunter SK-350TII machine for 120 seconds of mixing and degassing purposes. The mixer is capable to accommodate mixing and degassing for various materials regardless of any viscosity to achieve a homogeneous mixing. The mixing process is shown in Figure 3.2. The graphene was added at different percentage into the epoxy resin via three-roll mill to create shear force between the nanofiller.

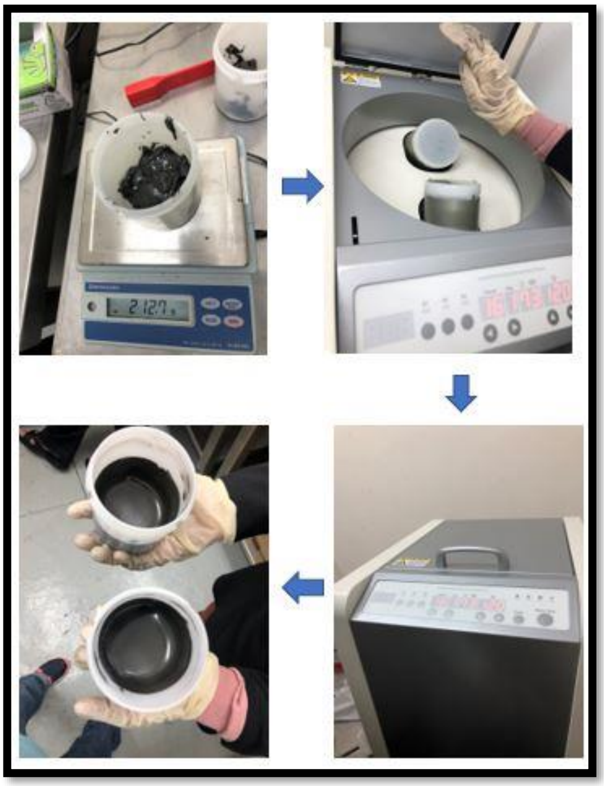


Figure 3.2: Mixing process by using Kakuhunter SK-350TII machine

The dispersion process took place right after the mixing process is completed using three-roll mill. The modified epoxy resin was then poured into the roller of three-roll mill EXACKT 80E machine. The calendaring process of the three-roll mill utilized the shear force created between the rollers to separate the agglomeration of graphene nanoplatelets and dispersing it as evenly as possible. The dispersion occurred for three times started with speed 200 m/s for the first and second round and increase to 350m/s. Figure 3.3 shows the calendaring process of three-roll mill and Table 3.1 summarize the configuration used for the calendaring process.

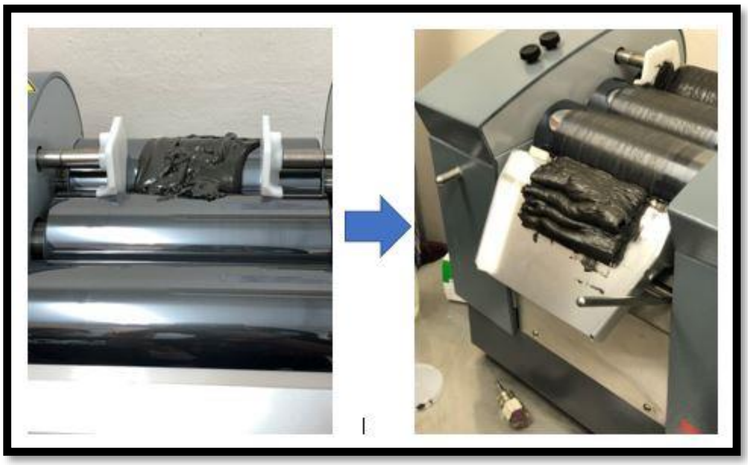


Figure 3.3: Dispersion of modified epoxy resin by using three-roll mill EXACKT 80E machine

Table 3.1: Design roller gap for three-roll mill

No of passes	**Gap 1 (μm)**	**Gap 2 (μm)**	**Roller Speed (rpm)**
1	100	60	200
2	60	30	200
3	45	15	350

The percentage of the graphene nanoplatelets begin with 0.01%. After that, according to ASTM D695 standards the epoxy grout was moulded into prism shape with dimension 12.7 mm x 12.7 mm x 50.8 mm for each specimen for compression test. The materials were also moulded into dog-bone shape for tensile test. According to ASTM D638 standards, the specimen will be of Type 1 specimen with dimensions 13 mm x 3.2 mm at the narrow section and thickness of 3.2 mm. The process was repeated with two other percentage of graphene nanoplatelets, 0.05% and 0.1%. Finally, the specimens undergo curing process at room temperature.

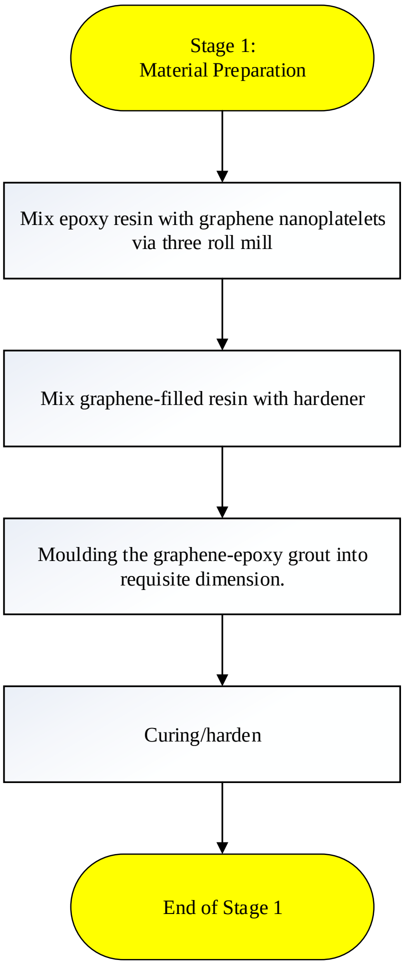


Figure 3.4: The process for stage 1

3.3 STAGE 2: MATERIAL TESTING

Stage 2 is the process for materials testing. Two laboratory tests were conducted to determine the mechanical properties of epoxy grout, which are compression and tensile test. The strength of the materials was determined accordance with ASTM D695. Figure 3.5 shows the flow chart of materials testing.

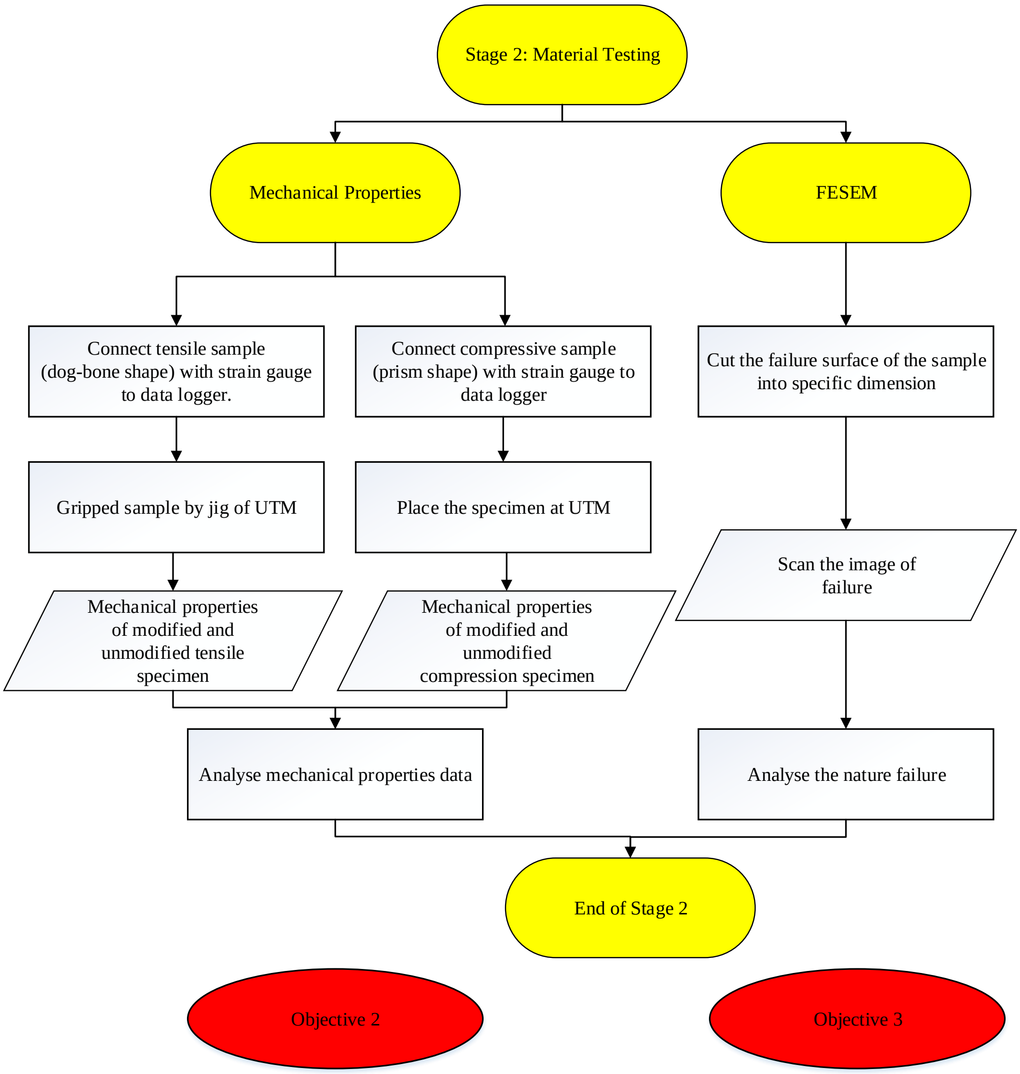


Figure 3.5: Flow chart of material testing.

After completing Stage 1, each compressive sample (prism shape) was glued using cyanoacrylate (CN) glue and connected to data logger where the strain readings were recorded. The specimen was placed at the Shimadzu Universal Testing Machine (UTM) and a loading rate of 1.3 (±0.3) mm/min was applied to the sample until failures occur. The reading of the load and strain were recorded by the computer data logger.

The steps of tensile test are similar with compression test. Tensile test has been conducted based on ASTM D638 standards. Every sample was connected with strain gauge and data logger where the readings were collected by the computer system. Next, the specimen (dog-bone shape) was gripped by the jig of the UTM while the crosshead movement was applied at 3.75mm/min's rate. The dimension of specimens was provided as input by the user into the UTM in order to obtain stress and strain reading. After the testing is completed, the failed sample was kept for further testing. The specimen considered fail when the failures occur at the weak point of the dog-bone shape. If the failures happen outside of the weak point of the specimen, the specimen will be rejected and the data of the specimen will deem as invalid, as specific by the standard. Figure 3.6 shows the UTM machine used for the mechanical properties test.

Figure 3.6: Universal Testing Machine

After the tests for mechanical properties are done, the failure part of the selected specimen of tensile test undergo FESEM test as shown as Figure 3.7. The nature of failure part of the specimen was studied and the small structure failure was visualized. The failure surface of the specimen was enlarged in nanometre scale under the microscope to have a better understanding and provide additional information of the failure surface of epoxy grout. To get the better visualization under the FESEM, a layer of Platinum coating was coated to the whole surface of the failure surface.

Figure 3.7: FESEM machine

3.4 STATISTICAL ANALYSIS

The test result of the mechanical properties was analysed by a series of statistical analysis. It started with the simplest form of statistics, the mean value, $\bar{x}$ where mean value of each property will be calculated. The function to get the mean value of the mechanical properties is to get the central tendency of the data. Eq. 3.1 is shown the equation of the mean value.

$$\bar{x} = \frac{\sum x_i}{n} \qquad \textit{Eq. 3.1}$$

Standard deviation, s, were obtained through a series of manipulations of the data set. The function of the standard deviation is to measure how the result spread out from the mean. Smaller value of standard deviation can reduces inaccuracy of the data. The equation of the manipulations is shown by Eq. 3.2.

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}} \qquad \textit{Eq. 3.2}$$

Coefficient of variation, CV is a simple measurement of variability of the data with respect to the mean. The CV is expressing the variation as a percentage of the mean and it is shown by Eq. 3.3.

$$CV\ (\%) = \frac{s}{\bar{x}} \times 100\% \qquad \textit{Eq. 3.3}$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

This chapter starts with result and discussion in regards to the mechanical properties of epoxy grout which are tensile and compressive properties. The behaviours of the grouts were investigated through stress-strain relationship and relates to the failure pattern of the grouts. In addition, the dispersion of graphene nanoplatelets in epoxy grout is discussed through the morphology image from FESEM test to understand the nature of failure.

4.2 MECHANICAL PROPERTIES OF MODIFIED EPOXY GROUT

4.2.1 Tensile test

Tensile properties are most important properties to be understood in pipeline rehabilitation because the stress that will cause failure in a pressurised pipe is in tension mode. The result of tensile strength for modified graphene is summarized in Table 4.1. Five specimens of modified graphene were studied under tensile test. The strength values presented in the table below are the average of the maximum stress of specimen when the failure occurred. The plus and minus sign (±) after the average value represent the standard deviation of the specimens. The tensile strength was observed to be ranged between 11MPa to 20MPa. As shown in Table 4.1, the tensile strength increase as the percentage of graphene nanoplatelets added into the epoxy resin increases. When comparing with the milled down specimen, the tensile strength of modified epoxy grouts shows increment of 46%, 64% and 88% for 0.01%, 0.05% and 0.1% of graphene added respectively as shown in Figure 4.1. In contrast to the strength, the Young's modulus of the milled down sample exhibits the highest Young's modulus in all the samples at 8.83 GPa. The 0.1% graphene sample has the highest tensile strength but the lowest Young's Modulus in all the graphene modified samples at 20.89 MPa and 6.67 GPa respectively. Based on the observed trend where the strength increase with the increase amount of graphene nanoplatelets, the percentage of graphene can be added more into the epoxy grout as the percentage will increase the tensile strength.

Table 4.1: Tensile strength of epoxy grout

Epoxy Grout	Tensile Strength (MPa)	Young Modulus (GPa)
Control	15.93 ± 0.36	8.65 ± 0.91
Milled down	11.09 ± 2.32	8.83 ± 2.52
0.01% of graphene	16.22 ± 8.18	7.15 ± 2.99
0.05% of graphene	18.18 ± 1.38	7.44 ± 1.88
0.1% of graphene	20.89 ± 8.09	6.67 ± 0.24

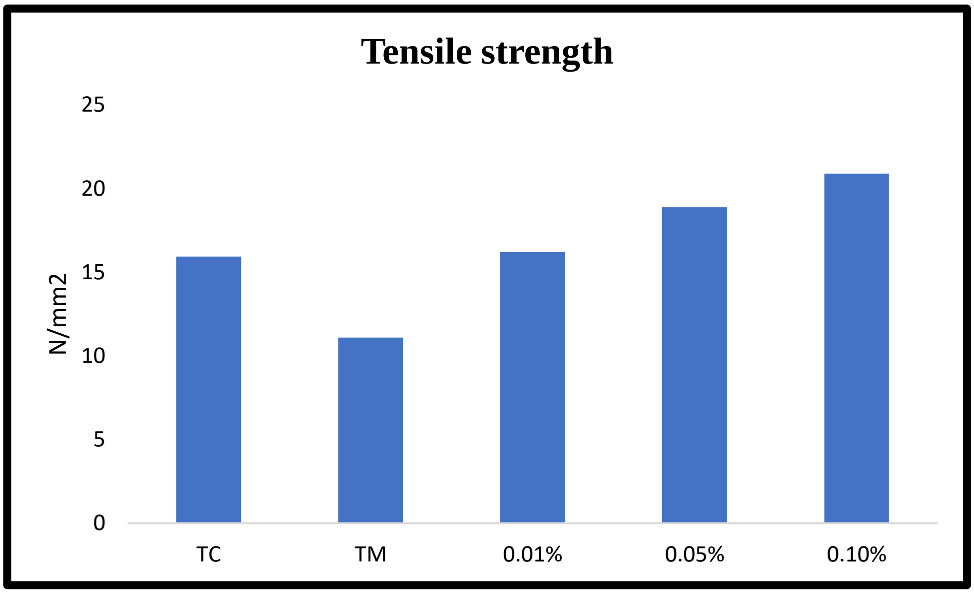


Figure 4.1: Tensile strength of epoxy grout

Figure 4.2 shows the stress strain relationship for tensile test. As can be observed in the figure, all graphene modified epoxy grouts exhibit a brittle behaviour without any plastic deformation detected in the stress-strain curve. Linear and slightly nonlinear elastic behaviour was observed for all grouts. No noticeable strain hardening or softening behaviour can be seen in the graph. All samples failed due to splitting, perpendicular to the loading direction during peak stress. Figure 4.3 shows one of the fractured samples in the tensile test. No noticeable deformation such as necking was observed in all samples.

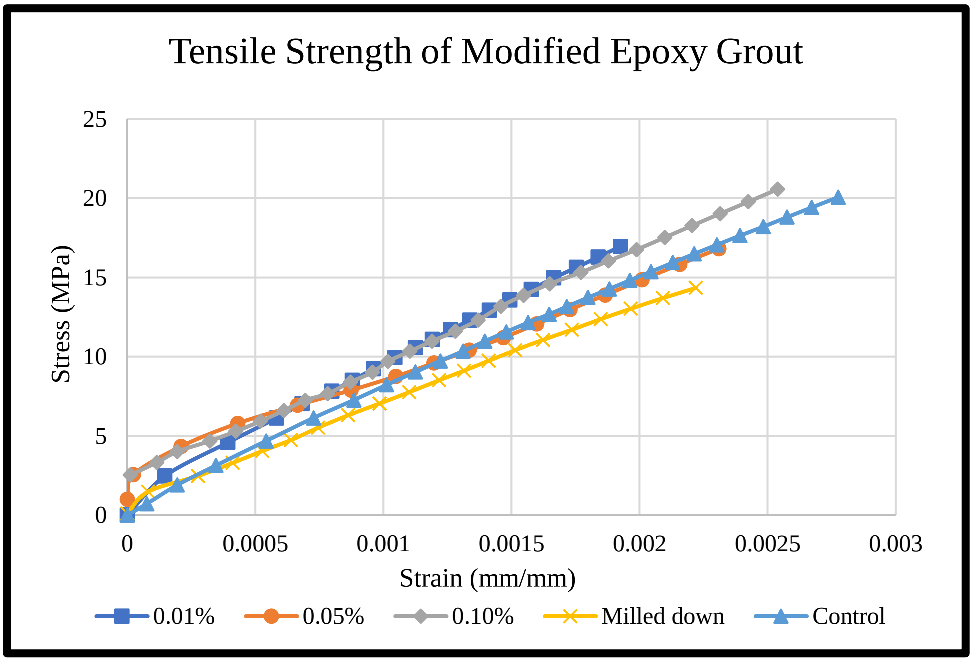


Figure 4.2: Stress-strain relationship of tensile strength

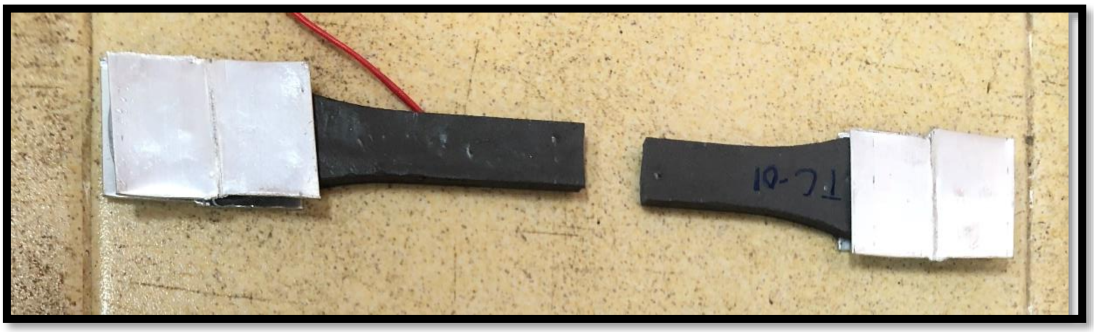


Figure 4.3: Failure pattern of tensile specimen

4.2.2 Compression test

Compressive strength of the infill material is brought onto action as the infill material act as the load transfer from the pipeline and the composite wrapping (Lim, 2017). The compressive stress and Young's Modulus of modified epoxy grout with different percentage was recorded as shown in Table 4.2. The compressive strength of all modified epoxy grout was found ranged from 71MPa to 82MPa. Besides that, the highest compressive strength is recorded at 82.67MPa which is sample with 0.05% graphene added to the epoxy grout. In contrast to the compressive strength, the Young's modulus of the milled down sample exhibits the lowest Young's modulus among all the samples at 7.21 GPa while 0.1% graphene sample has the highest Young's Modulus of graphene modified samples at 9.89 GPa but not in compressive strength. There is a 16% of strength increment as compared to milled down samples. The compressive strength of 0.1% and 0.01% graphene shows 3% and 14% increment when comparing with milled down sample, respectively. This shows that the optimum percentage for the compressive strength improvement is 0.05% for the tested graphene percentage. Figure 4.4 was summarized the pattern increment of the compressive strength.

Table 4.2: Compressive strength of epoxy grout

Epoxy Grout	Compressive Strength (MPa)	Young Modulus (GPa)
Control	69.19 ± 3.56	8.30 ± 1.59
Milled down	71.12 ± 5.56	7.21 ± 1.89
0.01% of graphene	80.80 ± 5.10	7.56 ± 0.89
0.05% of graphene	82.67 ± 6.83	8.14 ± 1.96
0.1% of graphene	73.02 ± 11.61	9.89 ± 0.62

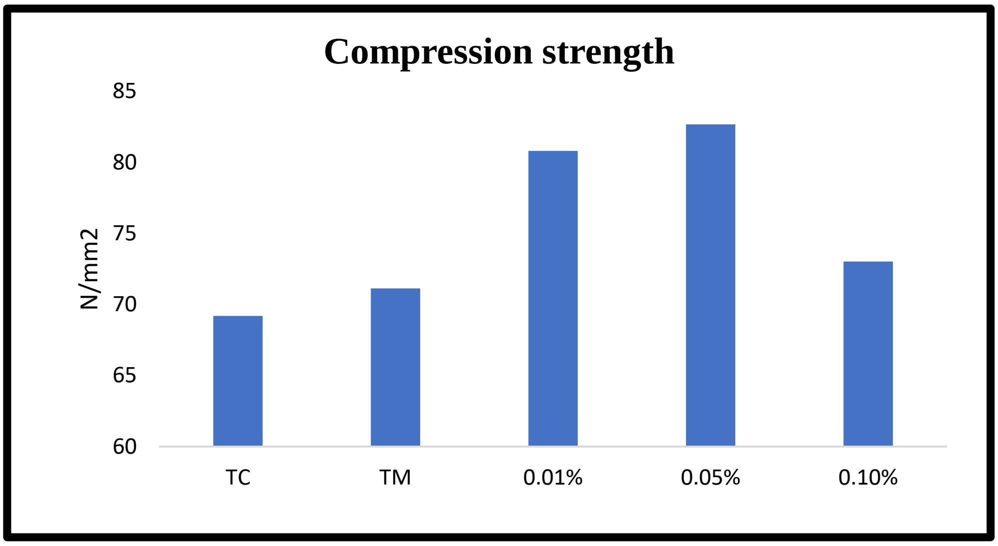


Figure 4.4: Compressive strength of epoxy grout

Figure 4.5 shows the stress strain relationship for compression test. As can be observed in the figure, all the graphene modified epoxy grouts represent linear graph exhibits elastic behaviour up to failure under compression load. There is also no noticeable plastic deformation can be detected in the figures. This signifies the brittle nature of the all samples. This finding is in contrast with Chen et al., (2002) where the authors defined that compressive stress strain behaviour of polymers have five stages, which is linearly elastic, non-linearly elastic, yield-like (peak) behaviour, strain softening, and nearly perfect “plastic” flow. The results in this study can be supported with close observation on the failure pattern of the sample. Figure 4.6 shows the failure pattern for compressive sample where a vertical crack was noticed at maximum stress.

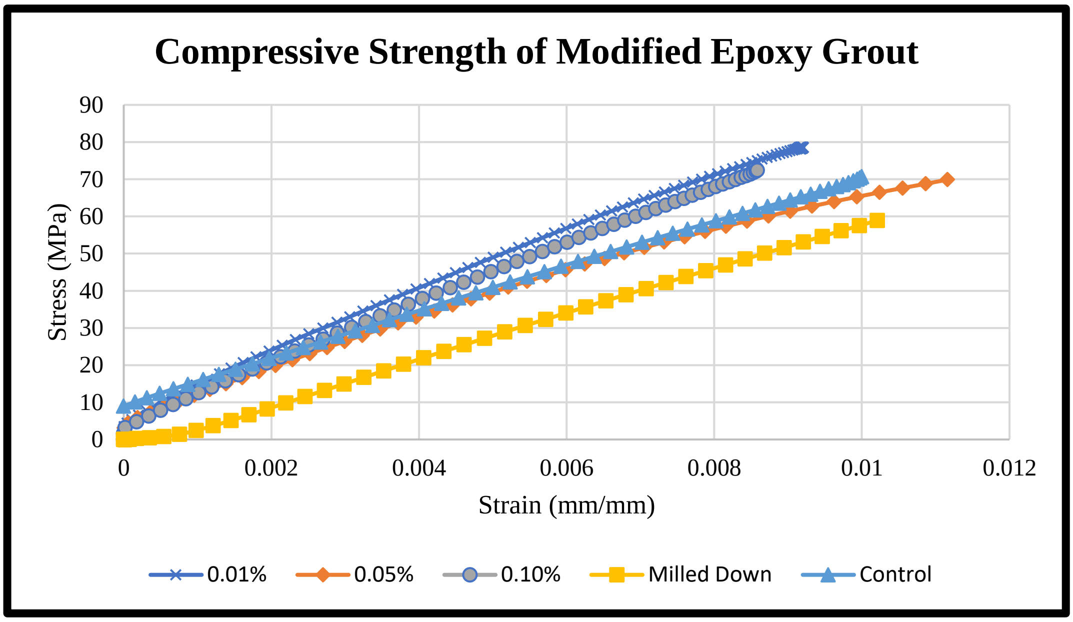


Figure 4.5: Stress-strain relationship compressive strength

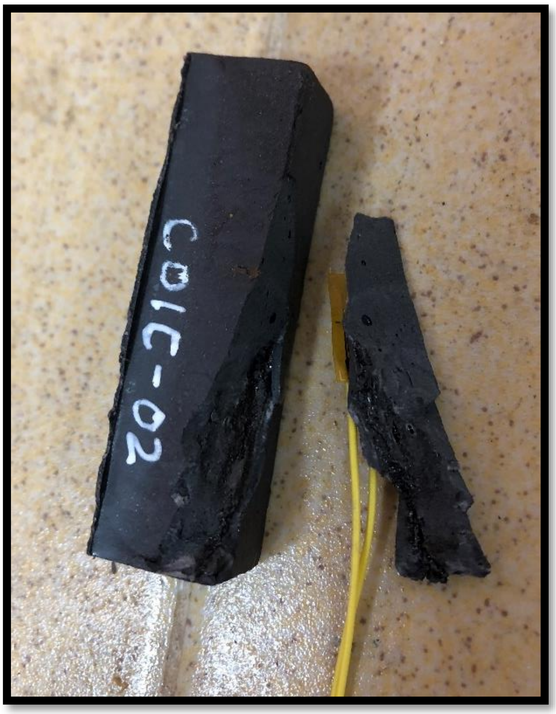


Figure 4.6: Failure pattern of compression specimen

There is a problem encountered during the calendaring process where the phase separation occurred. This is the reason why the result of the milled down sample is different as compared to control sample. Phase separation is a phenomenon where the existing reinforcement in epoxy grout separated from the epoxy grout by three-roll mill as shown in the Figure 4.7. The size of the existing reinforcement in the epoxy grout may be too big to go through the designated gap of the three-roll mill. The existing reinforcement in epoxy grout might be the main tensile strength contributor in the original epoxy grout. Hence, with the steel reinforcement which is the tensile strength contributor in the matrix separated from the epoxy grout in the milled down sample, the tensile strength drops dramatically from the control sample to the milled down sample. On the other hand, with the tensile strength contributor separated, the compressive strength of the matrix shows marginal increment because the matrix will be denser without any reinforcement.

Figure 4.7: Phase separation of the existing reinforcement on the three-roll mill

4.2.3 FESEM

Figures 4.8 show the result of the FESEM test on the failure surface of selected samples. FESEM was conducted to provide additional information on the failure surface of modified epoxy grouts. Samples of control, milled down, 0.1% of graphene (T10G-02) and 0.01% of graphene (T01G-03) were selected to undergo FESEM test. Sample T10G-02 and T01G-03 were selected to represent the highest and lowest percentages of modified epoxy grout, respectively. As shown in Figure 4.8, the graphene nanoplatelets in 0.1% sample is abundant on the failure surface while the 0.01% sample has less amount of graphene present on the failure surface. This shows that the sample of 0.1% graphene nanoplatelets contribute in the 88% increment of tensile strength while sample 0.01% show increment only 46% compared to milled down sample. On the other hand, the milled down sample does not have any graphene filler shows nothing on the failure surface. The control sample show the presents of existing steel filler compared to milled down sample which proves the phase separation on the three-roll mill.

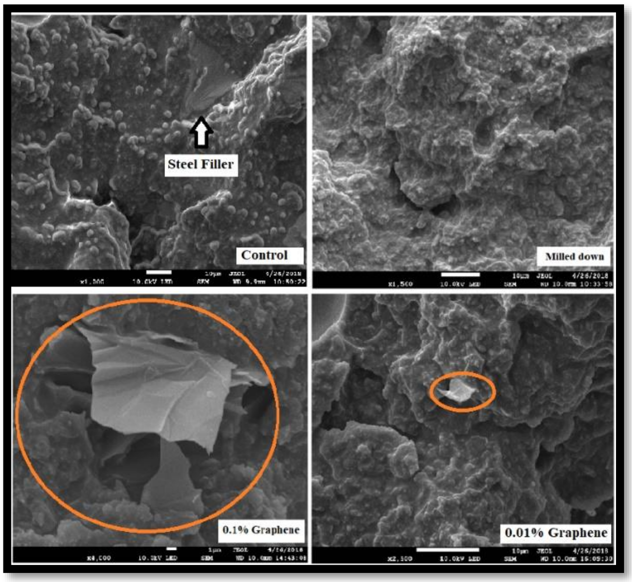


Figure 4.8: FESEM result of selected samples epoxy grout

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The following are the conclusions based on the three research objectives:

1. Mechanical properties modification has successfully achieved by adding 0.01%, 0.05% and 0.1% of graphene nanoplatelets into a commercially available epoxy resin. The dispersion of the nanofiller was done using calendaring technique via three roll mill and the modified samples show an increment for the tested properties.

2. Effect of graphene as reinforcement in epoxy grout has successfully investigated where the findings show the graphene filler has increases the strength of epoxy grout under tensile and compression test. Modified epoxy grout at 0.1% had recorded the highest tensile strength but the lowest Young's Modulus under tensile test compared to milled down sample. However, the compression test with 0.05% sample graphene added recorded the highest compressive strength. This shows that the graphene is a good reinforcement to increase strength for tensile test.

3. Finding in FESEM test shows the nature failure of the selected tensile sample. There are four types of samples were selected which is control, milled down, the highest and the lowest percentage samples of graphene where existing filler was found at the original commercially epoxy grout, abundant of graphene was found at the highest percentage and less graphene detected at lowest percentage of sample.

5.2 RECOMMENDATION

Recommendation for future research on improving the performance of epoxy grout is stated as follows:

1. Enhancement of the mechanical properties of epoxy grout should be done by using another type epoxy grout with no existing big size reinforcement inside the epoxy grout to ensure there is no problem encountered during calendaring technique.

2. Dispersion of graphene nanoplatelets is recommended to be carried out greater than three times rolling with smaller designated gap and suitable speed to get better homogenous dispersion.

3. Pre-mixing of graphene nanoplatelets and commercially epoxy grout is recommended using planetary centrifugal mixer (Kakuhunter SK-350II) before transferring into the three-roll mill machine (EXAKT 80E machine) to help achieve homogenous mixing instead of manually stirred using hand.

4. The findings in the study show the strength increment trend with higher amount of graphene added. This indicate the potential strength increase with higher percentages of graphene nanoplatelets, hence future works can be done by adding higher percentage of graphene nanoplatelets.

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