FYP - DISSERTATION

FAILURE ANALYSIS OF POLYVINYLIDENE FLUORIDE BY DEGRADATION FOR A PIPELINE

By

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Dissertation submitted in partial fulfilment of the requirements

for the Bachelor of Engineering (Hons) Mechanical Engineering

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

Dr Norlin Bt Nosbi

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BANDAR SERI ISKANDAR, PERAK

January 2020

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Ariff Razak

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ARIFF QAMARUDDIN BIN RAZAK

ABSTRACT

This present paper describes how polyvinylidene fluoride combats corrosion issue in pipeline of oil and gas industry. This study is crucial due to limited studies have been made upon polyvinylidene fluoride as a material for pipeline to prove its reliability and sustainability in the industry. Polyvinylidene fluoride will be tested upon its degradation over time. Tests will be executed upon the specimens of this material to prove that polyvinylidene fluoride has the better properties and favor compared to conventional materials in pipeline which are stainless and carbon steel. Upon this, the specimens of polyvinylidene fluoride will undergo tests to observe its water and chemical absorption at various parameters. Every samples of polyvinylidene fluoride will be tested upon its weight. This will show whether polyvinylidene fluoride is reliable due to its absorption rate. Study of this material will beneficial to oil and gas industry in future upon the reliability of polymers to sustain in oil and gas industry.

ACKNOWLEDGEMENT

Every student's project owns debt to their predecessors to their teachers, friends and their parents. I gratefully acknowledge my deep indebtedness to all of these.

The present work is an effort to throw some light on "**FAILURE ANALYSIS OF POLYVINYLIDENE FLUORIDE BY DEGRADATION FOR A PIPELINE"**. The work would not have been possible to come to the present shape without the able guidance, supervision and help to me by number of people.

With deep sense of gratitude, I acknowledged the encouragement and guidance received by Dr. Norlin binti Nosbi. I also convey my heartfelt affection to Mr. Mohd Jamalulhaq bin Mohd Pu'ad who helped and supported me during the completion of my thesis.

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TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATION

CHAPTER 1

INTRODUCTION

1.0 Background of Study

Corrosion exists as one of the issues that revolves in oil and gas industry. Oil and gas pipelines, refineries and petrol chemical plants often face serious corrosion problems. This is due to the present of water, carbon dioxide, and hydrogen sulfide. Furthermore, this issue may be aggravated by microbiological activity. The most crucial issue that influences corrosion rate is the multiphase fluids flow regimes. These conditions may be explained when at high flow rate, erosion-corrosion and flow-induced corrosion will occur, whereas at low flow rate, usual corrosion that has been found in pitting corrosion. Generally, corrosion is very related to the nature and amount of the sediments. This is due high-velocity flow is capable to sweep the sediment out of the pipeline. As for low velocity will allow sediments to settle at the bottom which provides sites for pitting corrosion to occur. This process will occur in any facilities that are available in this industry.

Corrosion is integral difficulty to be handled. There are three areas in which corrosion are critical which are economical concern, safety issues and resources conversations. Those leakages of hazardous supplies from a transport pipeline have the possibilities for serious and hazardous environmental impact, and fatalities to mankind. While pipelines are designed and developed to preserve their integrity, several factors such as corrosion may also make it challenging to maintain away from the incidence of leakage in a pipeline in the direction of its lifetime. On the specific hand, this facility needs to endure the danger of failure since it may face defects due to corrosion, erosion or fatigue due to fluctuating strain or temperature. Although pipeline on its safety concern has been enhancing over time, and human casualties, property loss, and environmental damage resulting from pipeline incidents are infrequent, but when they do show up the penalties may additionally be severe. For example, a 1999 liquid pipelines incident that occur in Bellingham, Washington, resulted in the launch of 277,000 gallons of fuel into a pass to the center of the town. This incident had precipitated three fatalities and injuring eight (Sosa & Alvarez-Ramirez, 2009).

Since the economic loss in the industry is extremely high, thus combating corrosion is very essential. There are various methods that are applicable supported with scientific studies to combat corrosion. Upon the methods, the use of corrosion inhibitor is one of the best and economical methods. It is broadly classified into anodic, cathodic or mixed corrosion inhibitor due to various types of corrosion inhibitors. In addition, they are also classified based on their chemical nature such as organic and inorganic inhibitors. The mechanism of this method is based on its capability upon chemical adsorption of the inhibitor on the metal surface and forms a protective thin film. This protects the underlying metal from corrosion. It also will lead to increase the potential of the metal surface. This is due to the metal enters the passivation region where a natural protective oxide film will form. Thus, the inhibitor may react with the corrosive component and remove it from the media (Rahuma & Kannan, 2014).

From the studies that have been made in recent years, the findings have proven that corrosion only can be delayed by decreasing the corrosion rate. These solutions are not capable to stop corrosion from occurring. This aspect is very crucial in pipeline due to this facility is used to transport crude oil and end products. Pipeline exists to connect refineries, terminal to the oil tanker ship and this will include distances and exposure to various environments. Most of the pipelines are fabricated from steel specifically carbon steel. Due to material selection, corrosion may occur due to electrochemical process that requires the simultaneous presence of moisture and oxygen. Thus, the present paper brings the idea by minimalizing corrosion by substituting the conventional materials to polymer and study its degradation. Polyvinylidene fluoride (PVDF) will be the subject for this study. This material is a semi-crystalline polymer that has been widely studied for its piezoelectric properties. This is due to its polar β phase. Besides that, the polar phase α, is also studied for its structural applications which yields the result to prove PVDF exhibits good mechanical properties and chemical resistance. The mechanical properties of this material have been studied by many authors, focusing on its analyzation of the macroscopic tensile and creep behavior over several strain decades and over temperature at large range (Challier et al., 2010). Nevertheless, upon the studies have been made before, the studies regarding the application of PVDF as pipeline are very limited since this material is widely used as piezoelectric in electrical appliances. Thus, the findings cannot prove the reliability of the material.

As conclusion, by this study of PVDF degradation, it is a hope for many studies will be made for corrosion issue. With these studies and researches, it holds the hope for future to combat corrosion in a better and efficient ways since corrosion is inevitable and may cause harm to mankind and environment.

1.2 Problem Statement

Corrosion is a very crucial to oil and gas industry since it may affect the asset reliability of a company since this issue in inevitable. Thus, it must be handled wisely by the engineers to ensure that the facilities may operate for a long time without having severe issue of corrosion. This study will mainly focus on corrosion in pipelines. This facility is widely fabricated by steel such as carbon steel and stainless steel. Over time, these materials may face corrosion and erosion due to the electrochemical reactions and flow of the liquid inside the pipelines where foreign particles may exist and affect their surfaces and resulting pitting which lead to thinning of the pipelines wall.

This study will be beneficial in the study of polymers in oil and gas industry. By having this substitution, corrosion might be minimal since there is no electrochemical process occurs and engineers will deal with degradation of the materials. PVDF has been claimed on its capabilities to substitute the application of metals in pipelines since the material is a thermoplastic that has properties of the ease of fabrication, good welding properties and high mechanical strength. Other than that, this material is also excellent in chemical resistant and high operating temperature. Due to limited studies have been made and lack of evidence to prove its reliability, thus is it wise for polymers specifically PVDF to be fabricated as pipelines to combat corrosion issue that revolves in this field?

1.3 Objective

To investigate PVDF degradation upon its claim by manufacturers to have excellent properties to combat corrosion and erosion by testing the material according to the parameters that are available in the environment of oil and gas.

1.4 Scope of Study

This study is designed to investigate PVDF alongside its characteristic and behavior. The intent of this study is to prove that PVDF is reliable to be applied for pipeline facilities in oil and gas industry. To obtain the results, tests will be conducted upon this material. The samples of PVDF will be complied upon American Society for Testing and Material (ASTM) standards. Those samples will be tested in liquid and gas environment. For liquid, PVDF will be exposed to different pH level; distilled water for neutral pH, acidic solution and seawater depending on its pH level. For gases, PVDF will be tested with carbon dioxide, CO_2. The intent of these tests observes the degradations and moisture absorption of this material when being expose to these environments.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

In the oil and gas industry, pipelines hold a huge role in the distribution of oil and gas. About 60 countries have about 2000 km of pipelines worldwide. Furthermore, it is estimated 10,000 km of new pipeline are planned to be installed in this decade which in 2005, it has cost $27 billion for 2500 km pipelines (Deffeyes, 2012). Pipeline may be fabricated in small or large size as it exists from 152.4 to 1219.2 mm in diameter. Most of these facilities are located underground and some of them are above the ground, such as pump stations. Pipelines network has been set up in Malaysia along this country for 2500 km. Malaysia has a small network of oil and gas pipelines, and tankers and trucks still rely on this state. Offshore oil fields Peninsular Malaysia are linked by the main oil pipelines to onshore storage and terminal facilities. It runs and finishes at the Kerteh plant in Terengganu from the Tapis pipeline. This also refers to the oil pipeline of Sabah and Sarawak, where the pipelines connect offshore with the Labuan and Bintulu oil terminals. An international oil pipeline operates from the Dumai oil refinery in Indonesia to the Melaka oil refinery and is an interconnecting oil product pipeline running from the Melaka refinery to the Klang Valley Distribution Terminal (KVDT) via Shell's Port Dickson refinery. This pipeline will be linked to the Pengerang Refinery launched by ARAMCO and Petronas in the latest development (Sovacool, 2011). There are wide range of products that exist in liquid tank. From onshore and offshore field, crude oil may be obtained as these crude lines will be transported to ports. Other than that, this oil is also being transferred to interconnecting point and refineries. Crude oil can be imported or imported domestically depending on its demand and suitability of its sulphur content. In addition, refined products such as gasoline, automotive diesel oil, kerosene and naphthalene also form part of the pipeline market. However, the pipeline also carries liquified natural gas (LNG) and liquified petroleum gas (LPG) and propane and all these gasses at normal temperature and pressure, but they are easily liquified when the pressure is applied (Pharris & Kolpa, 2012). Hence, this proves that pipelines play a big role in the oil and gas industry and they are a part of asset reliability that needs to be sustained.

2.2 Material of Pipeline

Most of the pipelines are using steel pipe to transport hydrocarbon. Most widely fabricated are stainless steel and carbon steel pipe. They are manufactured by accordance of the specifications of the American Petroleum Institute (API 1994, 2000). Furthermore, the American Society of Mechanical Engineers (ASME), the American National Standards Institute (ANSI) and the ASTM are being used as guidance too in manufacturing pipelines (Pharris & Kolpa, 2012). Due to this nature, corrosion is unavoidable since these materials contact with the crude oils, natural gas, petroleum products and environments. Crude oil has a complicated chemistry and it includes many factors that influencing its corrosiveness. These problems are hard to predicted since crude oil has different physicochemical composition. Total acid number (TAN), which includes total sulphur content, air, salt, and microorganisms, is normally classified as corrosiveness of crude oil. In different ways and phases, the application of these parameters and components affects corrosion. In instances, chemical compound such as hydrogen sulfide, H_2S and alkanethiols are corrosive to carbon steel. This will cause iron sulphide scale occurs. In addition, due to acid oxidation in this case, H_2S, which makes gas sour, this issue may cause general and pitting corrosion and hydrogen attack. Appear as latter blisters and cracks, H_2S can be released by cracking and can cause death when exposed to the atmosphere. Upon carbon dioxide, CO_2, the existence of this chemical is not corrosive when it is dry. But it can form carbonic acid, H_2CO_2 when it dissolves in air, and this compound is very water- corrosive. Furthermore, corrosion also can be induced through the presence of oxygen, O_2. Due to its activity under atmospheric pressure, this condition may occur, and air may enter the device during leakage or opening valve, which may cause corrosion. When reacting with hydrocarbon at high-temperature adsorption bed with water formation, the presence of O_2 in corrosion can result in pitting and affecting Stress Corrosion Cracking (SCC).

2.3 Corrosion in Pipeline

In Malaysia, it has been discovered that hydrogen sulfide, H_2S concentration and carbon dioxide, CO_2 are very high. These corrosive agents do encourage corrosion to develop in pipelines (Sass et al., 2015). A sum of $600 million was estimated to be spent annually in the oil and gas industry to fix and maintain corroded pipelines due to corrosion. Corrosion could cause huge economic costs and enormous damage to health, security and the environment without proper mitigation (Yuan et al., 2016). Corrosion may happen during the transportation of gas in pipelines where the water vapor will condense as the gas cools. This will lead CO_2 to dissolved in water and decrease the pH to 4. In some occasions, liquid water remains as thin layer on the inner surface of the upper part of pipe. As a result, it will cause severe localized corrosion. Shallow pits will form, and they will be accumulated with sharp surface areas. This occurrence happens when there is heat exchanged between the pipe and the cold environment such as seawater when the pipe is not thermally insulted. Since corrosion will lead to severity such as leakage which may bring harm to environments and mankind, mitigations must be taken. For H_2S, injection of H_2S scavengers and corrosion inhibitors which come from organic and cement coating and choosing the suitable alloy according to the standards may help in preventing SCC. For sweet corrosion, passive black film iron carbonate, $FeCO_3$ is formed under particular condition on the carbon steel surface and low-allow steel (to 9% Cr) may protect from corrosion but due high velocity stream and stresses, the protective iron carbonate may break. Thus, the effective to mitigate is by using martensitic stainless steels (>12% Cr) and caustic injection in controlled pH.

In corrosion that induced by oxygen, this chemical element must not exceed 10 ppmV. Despite this, presence of oxygen is crucial to keep protective oxide films. For wholesome corrosion cases, to mitigate, corrosion allowance addition is important to the thickness of the wall during design. Moreover, water vapor must be removed in natural gas and thermal insulation on the tube surface needs to be implemented. Other than that, thick organic coatings, vapor corrosion inhibitors and injection of corrosion inhibitors may help in preventing corrosion. Lastly, periodic cleaning using pigs is crucial in accordance to the inspection plan (Pharris & Kolpa, 2012). According to the "In-Line Inspection Systems Qualification Standard" API 1163, pigging is defined as a system driven through a pipeline for various internal activities (depending on the type of pig) such as fluid separation, cleaning or pipeline inspection. This method is applied to clean the pipeline while locating any wall thinning occurs along the pipeline. Thus, according to API570 for pipelines standards and inspections, mitigation action can be taken by cut and replace the pipelines that are affected by corrosion. In conclusion, these problems have been revolved in this industry for decades, thus latest technology and knowledge must be implied to sustain the business for future concern.

2.4 Non-Metallic Material in Oil and Gas

Technology has been evolved over the years and it affects oil and gas industry. The implementation of newest technology does help the equipment to have a longer lifespan since technology may combat corrosion issues. For decades, metals have been used for every equipment in this industry which will cause corrosion in long term usage. Thus, evolving technology has introduced oil and gas industry with non-metallic material options. From the studies have been made, the presence of non-metallic materials is also available worldwide. They have been applied in various facilities in the industry, in onshore and offshore as provided in Table 2.1.

TABLE 2.1. Non-Metallic Materials Application in Oil and Gas Industry

Non-Metallic	Place	Reference
Hydrogel polymer in enhance oil recovery (EOR)	Offshore	(Abidin et al., 2012)
Polyethylene coating	Pipeline	(Samimi & Zarinabadi, 2011)
Cross-linked polyethylene cable insulation	Submersible pumps in oil and gas wells	(Livingston et al., 2014)
Reinforced Thermoplastic Pipe in Saudi Aramco	Sour wells	(Bin Ziad et al., 2018)

2.5 PVDF Application in Pipeline

Since the application of steels in pipelines will lead to corrosion due to its nature under any circumstances, the substitution of metals with PVDF would be a better substitute as it has better properties based on the claims made by ARKEMA.

PVDF is a semi-crystalline polymer with an extended zigzag chain with a crystallinity of 35-70%. Consisting of PVDF that have insertion from head-to-tail, but there are also head-to-head and tail-to-tail defects. These may affect the houses with the crystallinity and PVDF itself. This fluoropolymer has several transitions and changed its own density for every polymorphic condition. Currently, there are five known states, *α, β, γ*, *δ* and *ε*. The most common phase that exists is *α*-PVDF with −70 ° C, −38 ° C(*β*), 50 ° C (*α*') and 100 ° C (*α*′) transitions.

Moreover, PVDF holds the characteristic that avoids most natural and inorganic chemical substances as opposed to chlorinated solvents. This will cause solid bases, amines, esters, and ketones attack this resin. In these conditions- based solvents, the stage of influence from swelling to complete dissolution. A wide range of polymers are compatible with PVDF. Commercially PVDF possesses the ability to blend with acrylic and methacrylic. As a result of radiation exposure, PVDF basically interlinks as ethylene tetrafluoroethylene (ETFE). Radiation from gamma rays will affect the mechanical residences of PVDF (Ebnesajjad, 2012).

In Prevent Corrosion's PVDF paper, PVDF is defined as a thermoplastic that characterized by its ease of processing, better welding properties, and good heat formability from other polymers. PVDF also has high mechanical strength at 35-55 MPa and possessed an excellent chemical resistance. It holds the capabilities for high operating temperatures at 120 °C. Other than that, this polymer is good as ultraviolet and gamma radiation resistor which makes PVDF has the characteristic of ageing resistance. Furthermore, this polymer can be designed and combined with any flanges, threaded and mechanical connections (Palovcak & Pomante, 2018).

Amid excellent claims regarding PVDF, it has not been developed for pipelines in the oil and gas industry. This study therefore intends to investigate PVDF and its degradation when exposed to the environment of oil and gas. While PVDF has great properties, it also suffers from several limitations. This is due to the free volume that presents in PVDF matrix. As results, PVDF will show membrane (selective barrier) characteristics (Goh et al., 2017). Such undesirable properties can result in the corroding agents being quickly penetrated for corrosion (Das & Prusty, 2013). To improve its anti-corrosion properties, nanofillers has been suggested. This process happens by reducing the pressure of contact and wettability. In addition, it will decrease water penetration and corrosive by increasing the tortuous pathway. Other than that, nanofillers also make the surface roughness become lower. This is good for the characteristic of being water and oil repellence (Nazari & Shi, 2016).

2.6 Study of PVDF in Pipeline Application

The study that has been made for PVDF is regarding the damage and fracture of unplasticized PVDF at 20 °C to applied for pipeline studies. The material has been studied by using different test geometries. Mechanical tests that have executed indicate that damage is essentially caused by void growth. Furthermore, the model has been observed to have instability on Double-Edge-Notched Tensile Specimen (DENT) which increases the stress and strains rates. This factor will trigger brittle fracture (Challier et al., 2010). The study may be helpful in the present paper to be guidance, but the limitation sets when the material used in the study is unplasticized PVDF. Thus, the constraints are different to the material that is used in present paper.

Despite having good reputation claimed by manufacturers, PVDF does not have established studies in application in pipelines. This material is widely used as a material in sensors due to its piezoelectric features. PVDF application as coating has shown its weakness due to its free volume in its matrix which allows corrosion to occur (Jing, 2017). Thus, the present paper holds the aim to prove the capabilities of PVDF application in pipelines. Tests and experiments will be conducted according to ASTM standards. This material will be tested upon its degradation to enlighten its reliability when it is being exposed to the simulated environments in the industry.

In conclusion, oil and gas industry has an unavoidable issue such as degradation. Therefore, by having this study, it is a hope that PVDF may be a better substitution for metals upon its excellent properties. Since PVDF may avoid ageing issue, this thermoplastic since it may save cost, manpower and any unexpected incident which may cause fatalities and injury.

CHAPTER 3

METHODOLOGY

3.1 Material

In this paper, PVDF had been processed according to ASTM D638: Standard Test Method for Tensile Properties of Plastics. The samples were processed according to the Type V of dog bone shape in the standard. Due to unavailability of facilities in the campus, the samples had been cut using manual notching machine that was available in Block 21, UTP. Due to the constraints, the samples could not be cut into dog bone shape. As results, the samples had been cut into rectangular shape as shown in Figure 3.1. The measurement of the samples was 63.5 mm in length and 3.18 ± 0.5 mm in width as shown in Figure 3.2. The samples were processed from 1 m^2 sheet to specified measurement according to the standard in three days. 50 samples altogether had been processed to undergo the test as planned.

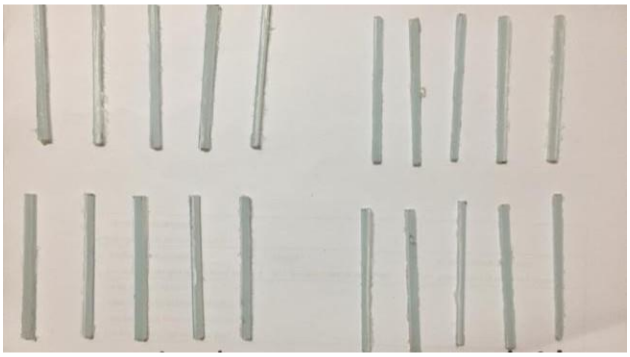


FIGURE 3.1. Samples Processed of PVDF

FIGURE 3.2. The Measurement of PVDF Samples

3.2 Water Absorption Test

In accordance of ASTM D570 for Standard Test Methods for Water Absorption of Plastic

This method would be tested upon submerged specimens in water in order to determine the water absorption relative level. This technique would be applied to examine plastics in all forms. This includes finished, hot-molded and cold-molded resin products. Laminated and homogenous plastics in rod and tube form and 0.13 mm (0.005 in.) or greater thickness plates was also applied. This standard also held two main focus:

1. As data on the proportion of water absorbed by a component, and consequently in such cases where the relationship between moisture and electrical or mechanical properties, measurements or appearance has been established as a guide to the effects of water exposure or wet preconditions on such properties.

2. As a deceptive test on a product's uniformity. This second feature refers to plate, pipe, and tube fingers when testing on the finished product.

The moisture content of a plastic material was closely associated with residences such as resistance to electrical insulation, dielectric losses, mechanical power, shape, and dimensions. The effect of water absorption on these properties was generally based on the type of exposure. This would include immersion in water or by way of exposing to excessive humidity. Such immersion experiments will be performed by using distilled water and seawater. Seawater was collected from Teluk Batik Beach, Lumut which was located in Perak at the coordinate of 4.1879° N, 100.6069° E. The samples were kept in the containers as shown in Figure 3.3.

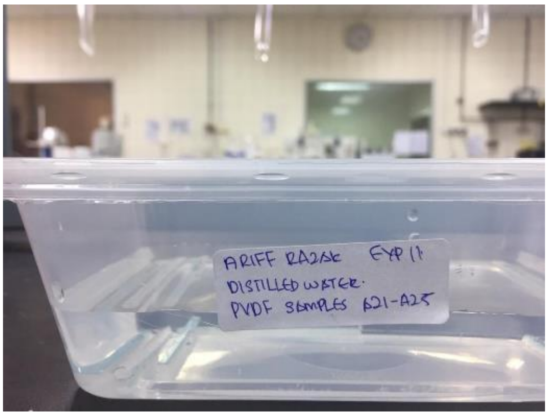


FIGURE 3.3. Samples of PVDF in Container

Procedure

Long-Term Immersion

The samples should be tested in order to determine the maximum water consumed when thoroughly soaked, cleaned the moisture with a dry cloth, immediately measured to the nearest 0.001 g and then put into the liquid. The test had been conducted for two weeks. The weighing had been repeated every day in the first week. It had proceeded by repeating every four days during the second week. The test had been indicated by three consecutive weighing, averages less than 1 % of the total weight expansion or 5 mg, whichever is higher; the sample shall then be considered to be substantially saturated. Once considerably saturated, the difference between the significantly saturated weight and the dry weight is known as the water absorbed. 10 samples of PVDF were prepared and kept in containers for this test. Five of the samples were immersed and soaked in distilled water while the others were immersed and soaked in seawater.

Calculation

The record had been included the values for each specimen, as follows, and the common values for the specimens:

a. The test samples measurement was 63.5 mm in length with 3.18 ± 0.5 mm in width in accordance of ASTM D638.

b. The test had been executed for two weeks and the samples were contained in room temperature.

c. The samples were fully soaked in the distilled water and seawater.

d. The weight of the samples was recorded every day in the first week and repeated every four days in second week.

e. The percentage increases in weight by immersion, measured as follows to the nearest 0.01 %.

f. The weight of the samples was calculated by the formula as shown in Equation 3.1 and determined to the nearest 0.01 %.

g. The results were determined by comparing the weight absorbed by the samples and represented in tables and charts.

$$Increase\ in\ weight, \% = \frac{wet\ weight - conditioned\ weight}{conditioned\ weight}\ X\ 100\% \qquad (3.1)$$

3.3 Chemical Test

In accordance of ASTM D543-95 for Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents

The practices of this standard covered the evaluation of plastic materials. This included cast, hot-molded, cold-molded, laminated resinous products and sheet materials to be tested for the resistance to chemical reagents. This also included the provisions for reporting the changes in weight, dimensions, appearance and strength properties of materials. Nitric acid and CO_2 were specified in the test to establish results on a comparable basis. The exposure of the samples was different according to its respective chemical reagent.

Nitric Acid

This chemical had been chosen for the test due to the availability of resource and fulfilling the capacity of FYP student. The concentration for nitric acid was 10% to be tested for the samples.

According to Chemical Resistance Chart from Plastic International, this source had identified that nitric acid of 10% concentration would cause slight attack by absorption. Thus, it would result some swelling and a small reduction in mechanical likely. The samples had been kept in glass container to ensure it did not affect by the corrosiveness of the acid as shown in Figure 3.4.

FIGURE 3.4. Samples Immersed in Distilled Water, Seawater and Nitric Acid

Carbon Dioxide

CO_2 corrosion is the most prevalent form of attack that has been countered in upstream operations. CO_2 exists in natural gas, crude oil and water which makes it is the most common environments in oil and gas industry. Sweet corrosion tends to occur in the form of pitting, uniform and galvanic corrosion (Kermani & Mohshed, 2003). Thus, CO_2 had been chosen to test the PVDF samples according to the suitability of FYP students.

250 ml hydrocarbon had been mixed with 250 ml distilled water as shown in Figure 3.5. This solution had been exposed in CO_2 in three different parameters. 15 samples of PVDF in total had been separated in three different containers for the parameters set. For the first parameter, the samples had been exposed at 1 bar pressure of CO_2 at 25°C. Next, the samples exposed at 20 bar pressure of CO_2 at 25°C. These parameters had been kept in a pressure vessel to seal the gas pressure as shown in Figure 3.6. For the third parameter, the samples had been exposed to 20 bar pressure of CO_2 at 60°C. This test executed in autoclave machine due to parameters set. All of these parameters were tested for five days.

FIGURE 3.5. PVDF Samples in Hydrocarbon and Distilled Water Mixture

Procedure

Long-Term Immersion

The samples should be tested in order to determine the maximum water consumed when thoroughly soaked, cleaned the ground moisture with a dry cloth, then immediately measure to the nearest 0.001 g and then immersed into the liquid. The test had been conducted for two weeks for the nitric acid while CO_2, the test had been executed for five days.

For nitric acid with 10 % concentration, the samples had been taken every day in the first week, then every four days in the second week. For CO_2, the weight would be taken at the start and end of the test.

The test had been indicated by three consecutive weighing, averages less than 1% of the total weight expansion or 5 mg, whichever is higher; the sample shall then be considered to be substantially saturated. Once considerably saturated, the difference between the significantly saturated weight and the dry weight is known as the water absorbed.

FIGURE 3.6. Pressure Vessel and Autoclave Machine Used for The Test

Calculation

The record had been included the values for each specimen, as follows, and the common values for the samples:

The test samples measurement was 63.5 mm in length with 3.18 ± 0.5 mm in width in accordance of ASTM D638.

a. The test had been executed for two weeks for nitric acid test and five days for CO_2 test.
b. 5 samples had been utilized for nitric acid with 10% concentration. For CO_2, 15 samples of PVDF were utilized for three parameters. The parameters were:

i. 1 bar of CO_2 at 25°C

ii. 20 bar of CO_2 at 25°C

iii. 20 bar of CO at 60°C

c. The samples were fully soaked in the solutions of nitric acid of 10% concentration. For CO_2, the samples were fully soaked in the mixture of 250ml of hydrocarbon and 250ml of distilled water. All the samples were kept in container and pressure vessels respectively.

d. The weight of the samples was recorded every day in the first week and repeated every four days in second week for nitric acid immersion test. For CO_2, the weight of the samples was recorded at the start and end of the test.

e. The percentage increases in weight by immersion, measured as follows to the nearest 0.01 %.

f. The weight of the samples was calculated by this formula as shown in Equation 3.1 and determined to the nearest 0.01%.

g. The results were determined by comparing the weight absorbed by the samples and represented in tables and charts.

3.4 Process Flow

Figure 3.7 illustrated the project flow of this studies. The methods that executed were complexed which the project started with literature review. Then, it followed with material preparation and experiments had been executed. Immersion and exposure test had been conducted on all of the PVDF samples. The results and discussions of this project had been represented by tables and charts. Lastly, conclusion had been made to decide whether the objective this study had been reached. These process flows would determine the success of this studies.

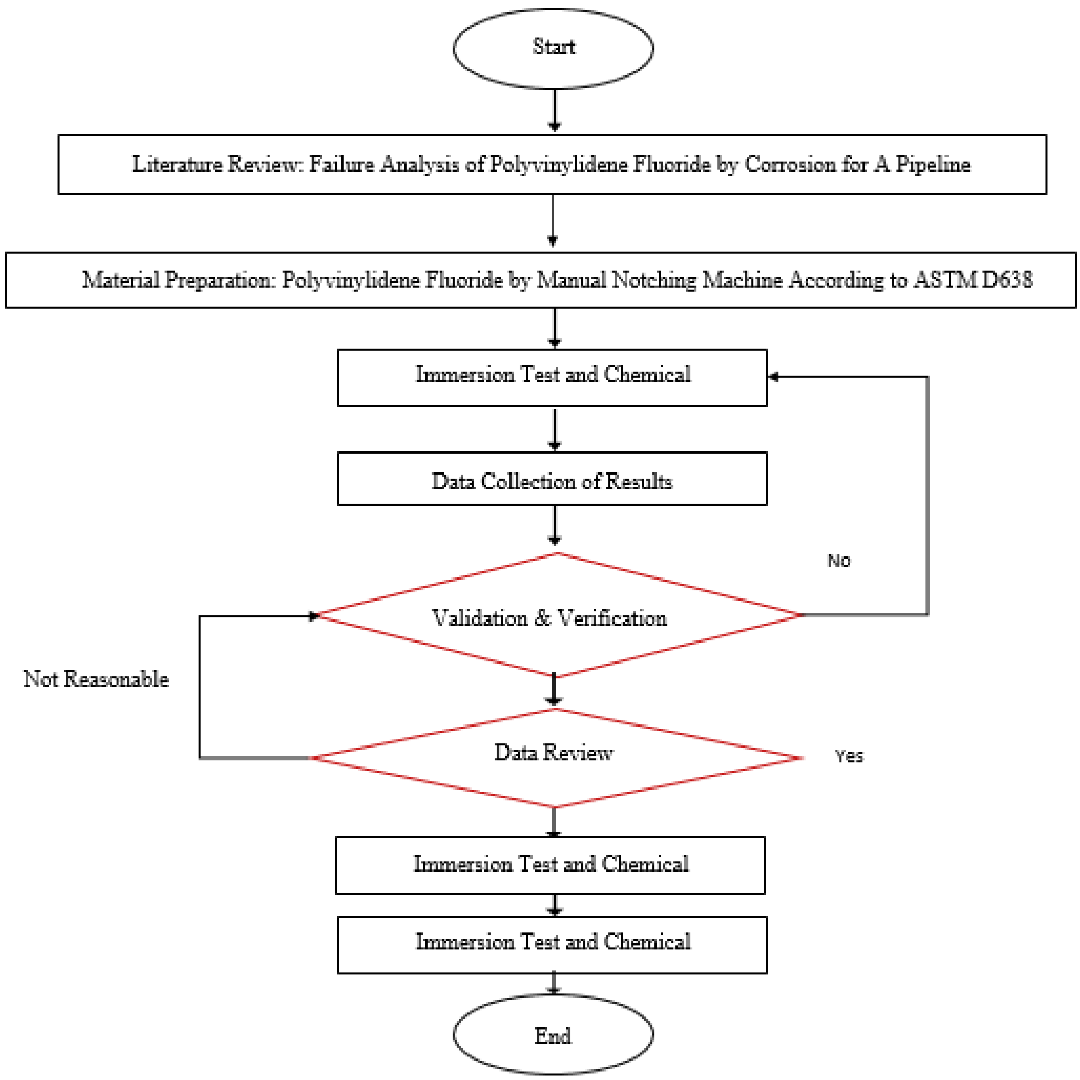


FIGURE 3.7. Process Flow of the Study

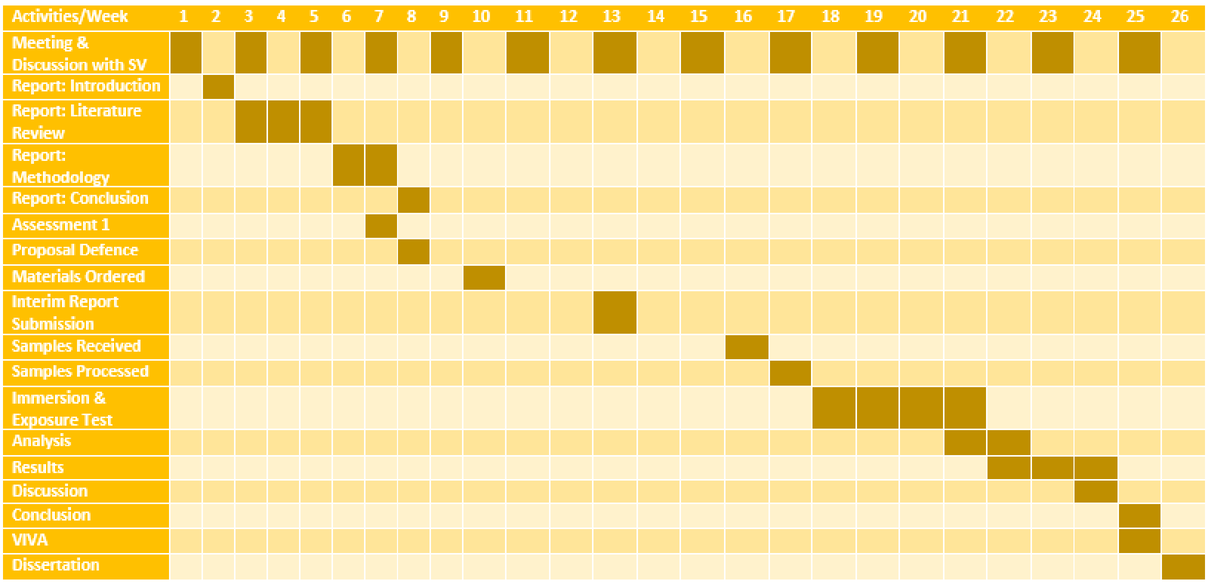
3.5 Project Milestone & Gantt Chart

The present paper had been planned throughout two semesters to be executed as shown in Table 3.1 and Table 3.2.

TABLE 3.1. Project Milestone

Activities	Date
Safety Lab Briefing	25 January 2020
Materials Processed (50 Samples) - Processed by manual notching machine - Specification upon ASTM D638 Type V	30 January 2020
Start of Experiment (Chemical & Water Absorption Test) - Samples weighted and kept in containers - Test ran for 14 days	14 February 2020
End of Experiment - Samples weighted and average weight had been taken - Difference of weights had been measured	3 March 2020
Completion of Data Analysis	15 March 2020
Completion of Documentation and Viva	5 April 2020

TABLE 3.2. Gantt Chart



CHAPTER 4

RESULTS AND ANALYSIS

4.1 Immersion Test

This test had been done according to ASTM D570: Standard Test Methods for Water Absorption of Plastic. Five samples of PVDF were immersed in three solutions each, which compromised distilled water, seawater and nitric acid with 10% concentration.

4.1.1 Distilled Water Immersion

The weights of the PVDF samples had been recorded and represented as shown in Table 4.1 and Figure 4.1.

TABLE 4.1. Weight Reading of PVDF in Distilled Water

Day/Samples(g)	**Day 0**	**Day 1**	**Day 2**	**Day 3**	**Day 6**	**Day 10**	**Day 14**	**%**
A21	1.271	1.272	1.272	1.272	1.273	1.274	1.275	+0.31
A22	1.129	1.130	1.130	1.130	1.130	1.131	1.132	+0.27
A23	1.319	1.320	1.320	1.321	1.321	1.321	1.322	+0.23
A24	1.262	1.262	1.262	1.262	1.263	1.263	1.263	+0.08
A25	1.029	1.029	1.029	1.029	1.029	1.030	1.031	+0.20
Average	1.202	1.203	1.203	1.203	1.203	1.204	1.205	+0.25

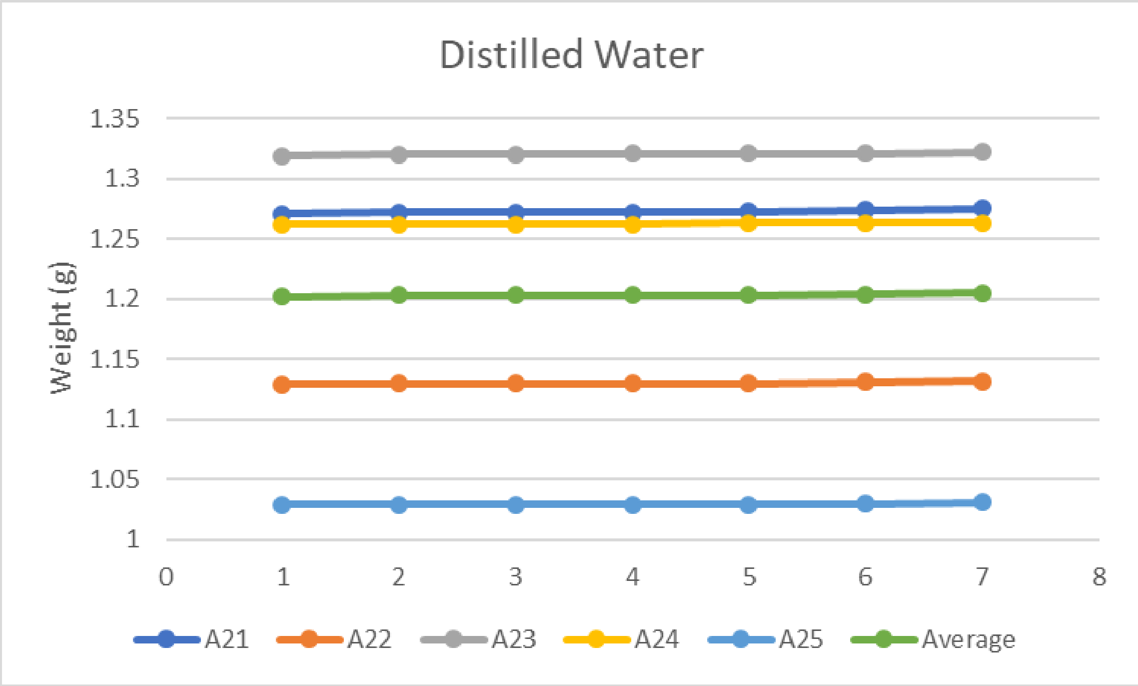


FIGURE 4.1. Weight Reading of PVDF in Distilled Water

From the results that had been collected, the samples weights were increasing. The average results had shown increment 0.003 g at 0.25%. PVDF was known for being hydrophobic fluoropolymer. This characteristic contributed to its low water absorption. Thus, the percentage of water absorption were relatively low. As results, the absorption rate of the samples was very low.

4.1.2 Seawater Immersion

The weights of the PVDF samples had been recorded and represented as shown in Table 4.2 and Figure 4.2.

TABLE 4.2. Weight Reading of PVDF in Seawater

Day/Samples(g)	**Day 0**	**Day 1**	**Day 2**	**Day 3**	**Day 6**	**Day 10**	**Day 14**	**%**
B21	1.089	1.090	1.090	1.090	1.090	1.090	1.091	+0.18
B22	0.919	0.920	0.920	0.920	0.921	0.921	0.922	+0.33
B23	1.075	1.075	1.076	1.076	1.076	1.076	1.076	+0.09
B24	1.059	1.060	1.060	1.061	1.061	1.061	1.061	+0.19
B25	1.014	1.015	1.015	1.015	1.016	1.016	1.017	+0.30
Average	1.031	1.032	1.032	1.032	1.033	1.033	1.033	+0.19

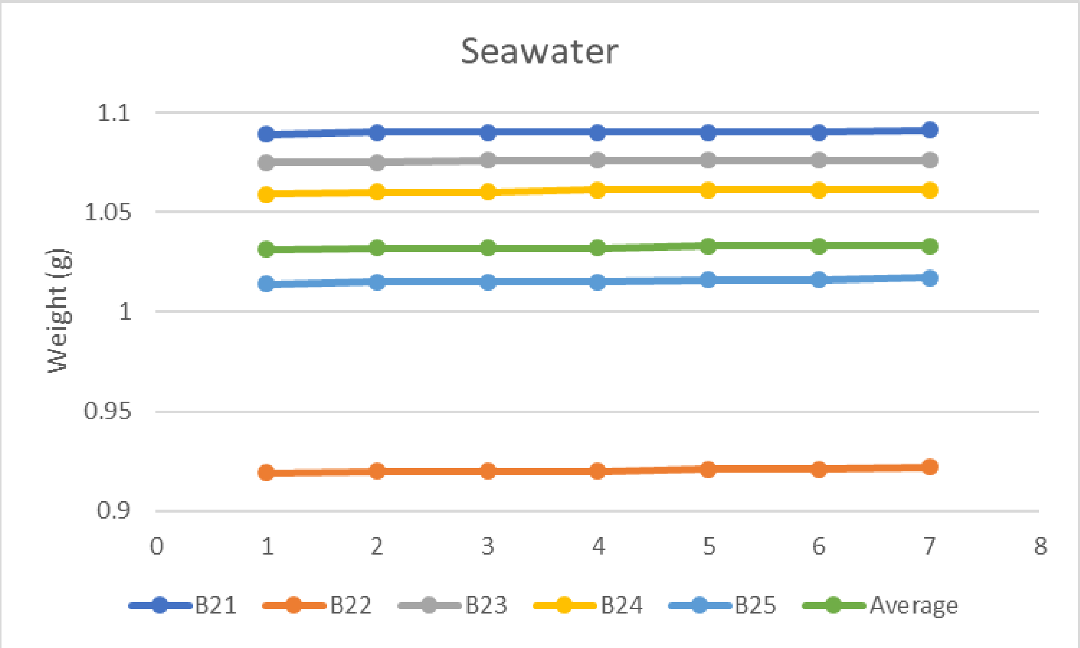


FIGURE 4.2. Weight Reading of PVDF in Seawater

From the results that had been collected, the samples weights were increasing. The average results had shown increment 0.002 g at 0.19%. Due to being hydrophobic fluoropolymer, this characteristic contributed to its low water absorption. Thus, the percentage of water absorption were relatively low. As results, the absorption rate of the samples was very low. The seawater has the pH of 8.22 as shown in Figure 4.3, thus seawater was an alkaline solution. Even though, the solution was alkaline, it did not affect the samples weight. Thus, it proved that PVDF had high resistivity to its surrounding.

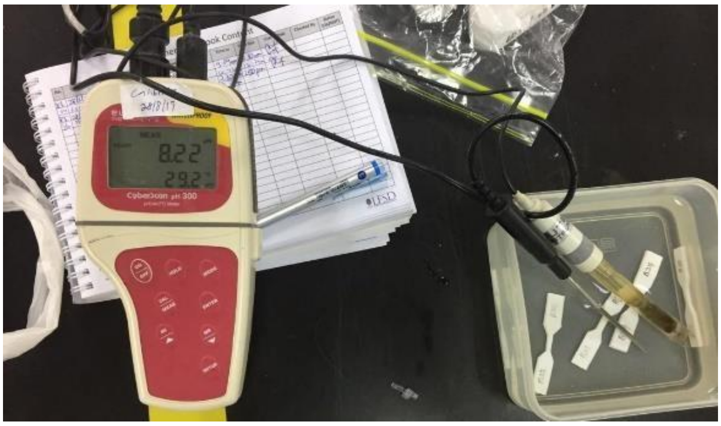


FIGURE 4.3. pH Reading of Seawater

4.2 Chemical Exposure Test

This test had been done according to ASTM D543-87: Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents. Samples were tested in nitric acid with 10% concentration with the same procedure as immersion test. In addition, five samples of PVDF were immersed in a mixture of 250 ml of hydrocarbon and 250 ml of distilled water solution. Then, this samples in the solution were exposed to CO_2. There were three parameters that had been done in the tests.

4.2.1 Nitric Acid Immersion

The weights of the PVDF samples had been recorded and represented as shown in Table 4.3 and Figure 4.4.

TABLE 4.3. Weight Reading of PVDF in Nitric Acid 10% Concentration

Day/Samples(g)	**Day 0**	**Day 1**	**Day 2**	**Day 3**	**Day 6**	**Day 10**	**Day 14**	**%**
C21	1.135	1.135	1.136	1.136	1.136	1.136	1.137	+0.18
C22	0.996	0.997	0.998	0.998	0.998	0.999	1.001	+0.50
C23	1.088	1.089	1.089	1.090	1.090	1.090	1.090	+0.18
C24	1.032	1.032	1.032	1.033	1.033	1.034	1.035	+0.29
C25	0.900	0.901	0.901	0.901	0.902	0.902	0.903	+0.33
Average	1.030	1.031	1.031	1.032	1.032	1.032	1.033	+0.29

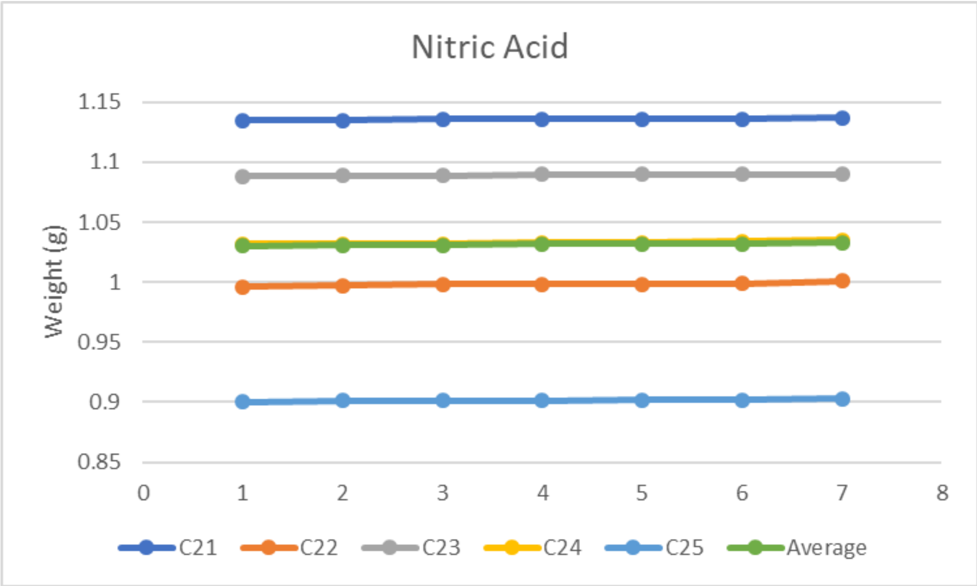


FIGURE 4.4. Weight Reading of PVDF in Nitric Acid 10% Concentration

From the results that had been collected, the samples weights were increasing. The average results had shown increment 0.003 g at 0.29%. The percentage of water absorption were relatively low due its characteristic for being hydrophobic fluoropolymer. As results, the absorption rate of the samples was very low. The nitric acid solution has the pH of 3.01, thus this solution was very acidic. It was tested with 10% concentration of nitric acid since according to Chemical Resistance Chart made by Plastic International, they recommended this concentration since it caused slight attack by absorption. Furthermore, it caused some swelling and a small reduction in mechanical likely. Even though the solution was acidic, it did not affect the samples weight by having reduction in weight due to corrosive solution. This showed that PVDF was having high resistivity due to its capability to withstand the acidity of the nitric acid solution during the study period.

4.2.2 20 Bar of CO_2 at 25 °C Exposure

The weights of the PVDF samples had been recorded and represented as shown in Table 4.4 and Figure 4.5.

TABLE 4.4. Weight Reading of PVDF Samples in CO_2 Exposure

Time/Samples(g)	Start	End	%
D21	1.007	1.003	-0.40
D22	1.083	1.079	-0.37
D23	0.997	0.992	-0.50
D24	1.211	1.205	-0.50
D25	1.154	1.150	-0.35
Average	1.090	1.086	-0.37

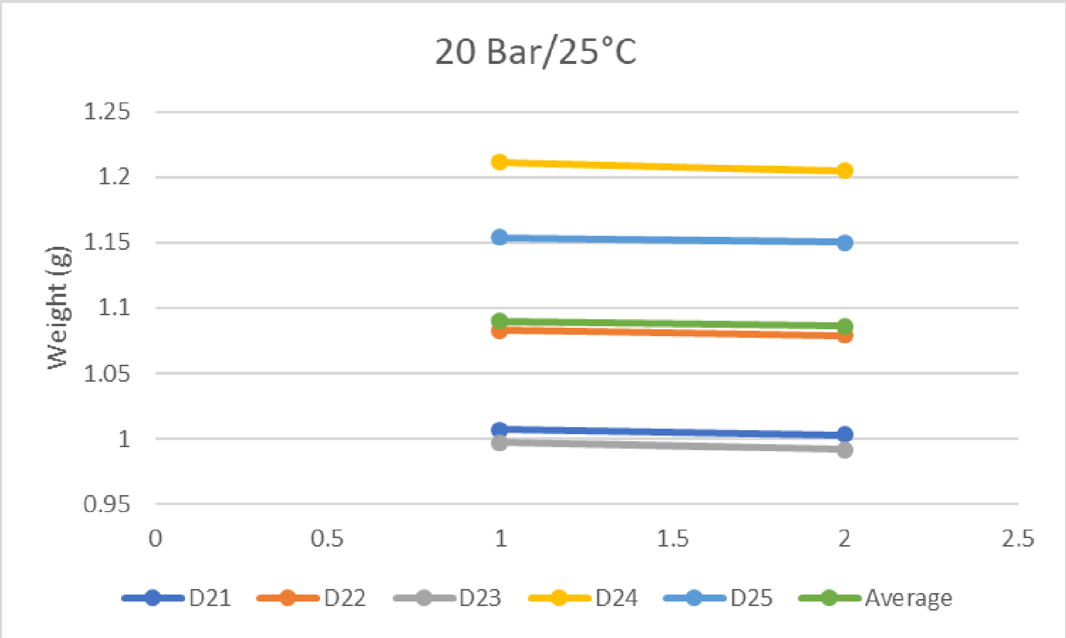


FIGURE 4.5. Weight Reading of PVDF Samples in CO_2 Exposure

From the results that had been collected, the samples weights were decreasing. The average results had shown decrement 0.004 g at -0.37%. The changes were minimal as PVDF possessed the characteristic to have chemical inertness. During the test, there was leakage that detected on the third day which made the pressure of CO_2 decreased. Due to this constraint, CO_2 gas supply had been supplied continuously to ensure that the samples were receiving sufficient pressure of CO_2 according to the parameter given. The results might be unreliable for this study due to technical failure occurred.

4.2.3 1 Bar of CO_2 at 25 °C Exposure

The weights of the PVDF samples had been recorded and represented as shown in Table 4.5 and Figure 4.6.

TABLE 4.5. Weight Reading of PVDF Samples in CO_2 Exposure

Time/Samples(g)	**Start**	**End**	**%**
F21	0.949	0.942	-0.74
F22	1.169	1.16	-0.77
F23	0.921	0.914	-0.76
F24	0.999	0.992	-0.70
F25	0.942	0.935	-0.74
Average	0.996	0.989	-0.70

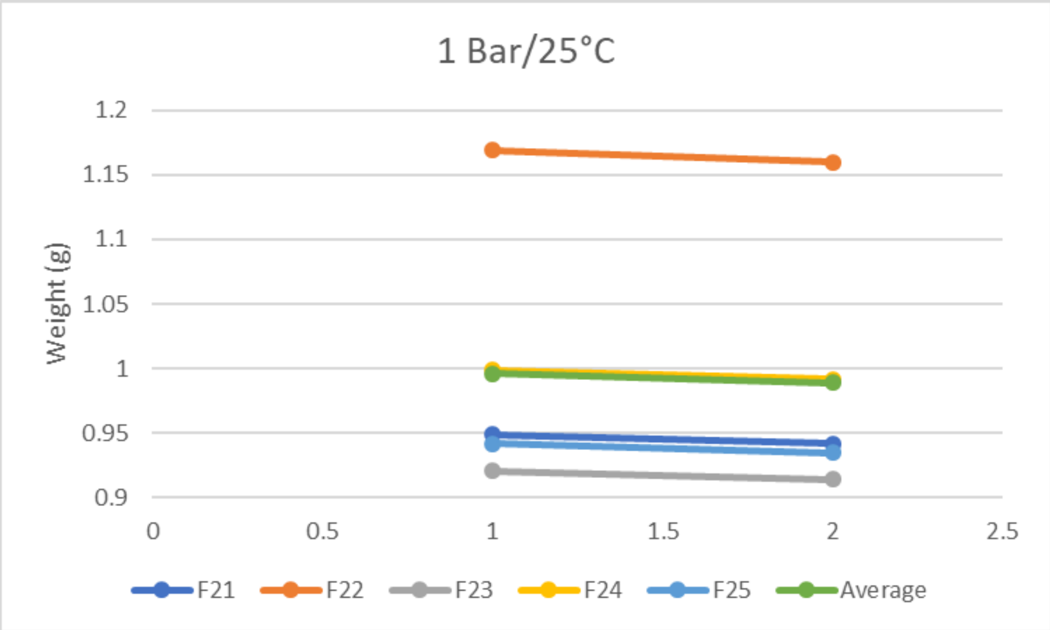


FIGURE 4.6. Weight Reading of PVDF Samples in CO_2 Exposure

From the results that had been collected, the samples weights were decreasing. The average results had shown decrement 0.007 g at -0.70%. The changes were minimal due to PVDF characteristic was chemical resistance material. During this test, there was no incident that may affect the results such as leakage. The results showed that PVDF could sustain under pressurized CO_2 environment due to little amount of loss.

4.2.4 20 Bar of CO_2 at 60 °C Exposure

The weights of the PVDF samples had been recorded and represented as shown in Table 4.6 and Figure 4.7.

TABLE 4.6. Weight Reading of PVDF Samples in CO_2 Exposure

Time/Samples(g)	Start	End	%
G21	1.331	1.334	+0.23
G22	1.038	1.042	+0.39
G23	1.084	1.088	+0.37
G24	1.095	1.097	+0.18
G25	0.995	1.000	+0.50
Average	1.109	1.112	+0.27

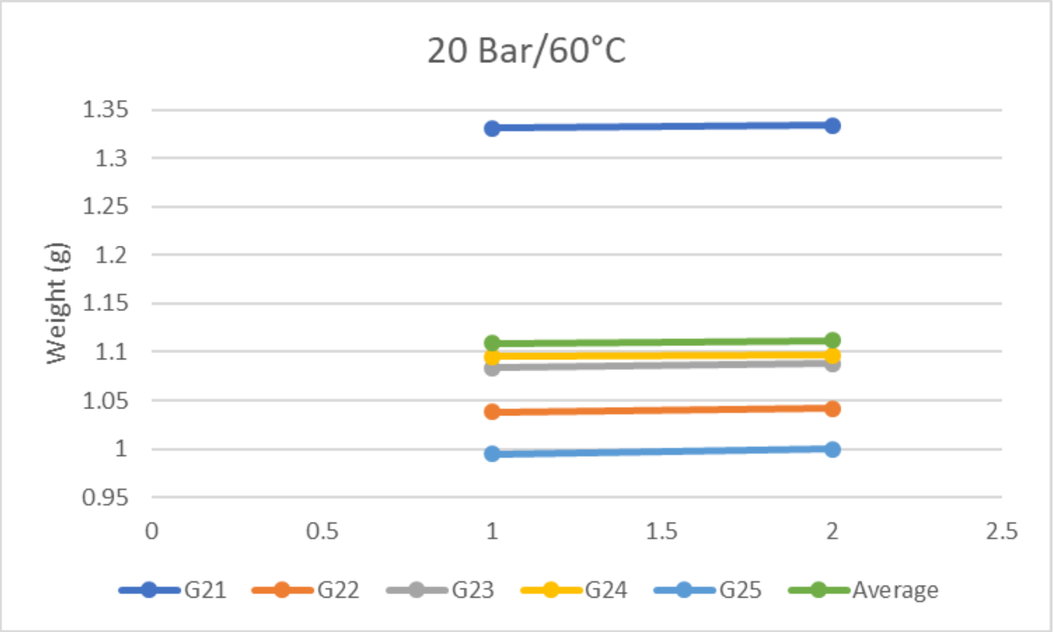


FIGURE 4.7. Weight Reading of PVDF Samples in CO_2 Exposure

From the results that had been recorded, the samples weights were increasing. The average results had shown increment 0.003 g at 0.27%. The changes were minimal as PVDF possessed chemical resistance characteristics. These results might have been affected by the technical faulty that happened in the autoclave machine during the study period of these samples. The machine had rose to 100°C before dropping to 30°C before being stable at 60°C according to the parameter given. As results, despite the weights were increasing due to exposure, but the samples melted at the edge due to the high temperature in the autoclave. The results might be unreliable for this study due to technical failure occurred.

4.3 Shapes, Size and Angle

4.3.1 Post Test Samples

FIGURE 4.8. The Measurements of the Post Test PVDF Samples

The samples had been shown that there were no any changes in terms of sizes, shapes and angles despite underwent different parameters that caused reduction and increment in weights. All the samples still had the same 63.5 mm in length and 3.18 ± 0.5 mm in width. Moreover, no angles changed and still remained at 0° as shown in Figure 4.8.

4.4 Project Limitation

The study had been planned and executed in two semesters for Final Year Project. Within this duration of study, it had been found that there were limitations for this study to fully achieve its objective. Firstly, the degradation study of PVDF in oil and gas was a complex title which complex methodology was needed in order to execute the study perfectly. It was important in this study to prove this material could sustain in oil and gas industry. PVDF should be proven that it was a better material than conventional materials that had been used such as carbon steel. But due to limitations and capacity of a FYP student, the execution could not be done fully. Initially, the study should include H_2S exposure due to sour corrosion that were most likely to happen in the industry. Due to safety concern, this exposure test could not be proceeded, and this would likely cause some lack of evidences that PVDF was reliable to be applied in the industry.

The limitations also came in terms of facilities. The material of PVDF had been received in the size of 1 m^2. The process to cut the material should be done by moulding to achieve the dog bone shape specifically according to ASTM D638. Due to lack of facilities, the process could not be executed, thus alternative way had been done. PVDF sheet was processed by manual notching machine. As results, the samples made were not perfect as intended. The final shape of the samples had been processed in rectangular shape instead of dog bone due to this constraint. This limitation would affect the tensile test in further analysis of this study.

Next, technical failure that occurred during the study also might cause the unreliability of this study. Autoclave machine that supposed to contain the samples at 20 bar pressure of CO_2 at 60°C faced technical failure during the test. The temperature of the autoclave machine had risen to 100°C which caused the increment of the pressure. This would likely damage the samples and the objective of the test could not be achieved.

Lastly, due to nCOVID-19 which had caused pandemic around the globe, the study of PVDF degradation had been discontinued. This was due to the Movement Control Order (MCO) by the Malaysian government had limited this study. The campus had been shut down and no further analysis could be executed. Thus, further test and analysis that had been planned initially such as hardness and tensile test could not be done. Furthermore, X-Ray Diffraction and Energy Dispersive X-Ray Spectroscopy in the analysis of Scanning Electron Microscopy (SEM) could not be executed due to this restriction. Thus, the lack of tests and analysis in this study might affect the reliability of the PVDF study.

As conclusion, the objectives might have been reached with the progress that had been done. But due to the limitations that occurred during the study, it would cause lacks evidence to introduce PVDF into oil and gas industry since the sustainability and reliability could not be proved wholly.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

The study of the failure analysis of PVDF by degradation for a pipeline had concluded that this material has the potential to shine in the future. Based upon the results achieved in the results of the tests, it could be proven that the absorption of PVDF samples were relatively low. These results might be supported due to PVDF was widely known as hydrophobic polymer. By having this characteristic, this meant that the material might resist the absorption of water. Due to this factor, the all of the samples were successfully passed the immersion and exposure tests by having only less than 1 % absorption in two weeks.

The objective of the study could be successfully achieved. By this study, it had shown that the samples of PVDF had the potential to combat corrosion that revolved in the oil and gas industry. This was due to low absorption rate of the samples and no damage had been observed on the samples as they were still in the initial shape with the same measurement. The results had been proved that PVDF was an excellent material that could sustain in neutral, alkaline and acidic environments with no harm. Moreover, PVDF also was reliable to survive in sweet corrosion environment due to the results that had been yielded in the CO_2 exposure test.

Application of polymers especially PVDF shall have lots of studies to prove its reliability and sustainability in future. This might benefit the oil and gas industry since the material possesses better characteristics compared to the conventional materials. Upon this study, the limitations and recommendations of this study shall be considered as lesson learned to achieve an excellent study in the future.

5.2 Recommendation

The present paper had been done as an early study of PVDF in the application of oil and gas industry, there were points that might be improved in future. Polymer study would be crucial in future since these materials would be pioneers in the industry. This initiative might be beneficial to this industry since the sustainability of the PVDF would combat corrosion and being a better substitution for the conventional material that had been used currently.

To objective of this study would be solidly achieved when the facilities provided should be improved to be competent to execute the study. By having excellent machines such as molding machine, the samples of PVDF should have the perfect dog bone shape. This initiative would be effective since the tensile test would yield accurate results. In addition, the autoclave machine should be improved on its performance. PVDF samples could be proven to be sustained at high temperature when the autoclave machine performed perfectly as planned. Due to leakage of the machine and technical faulty, the results of this parameter could not prove the sustainability of the samples.

As conclusion, the recommendations that had been concluded upon this study would improve better studies in future.

REFERENCES

Abidin, A., Puspasari, T., & Nugroho, W. (2012). Polymers for enhanced oil recovery technology. *Procedia Chemistry, 4*, 11-16.

Beaumont, J. (2017). *Non-Metallic Piping Systems for Corrosive Fluid Handling.* Paper presented at the CORROSION 2017.

Bin Ziad, A., Subaii, A., Alshammari, F., Buali, M., & Fazaa, J. (2018). *The First Application of the Reinforced Thermoplastic Pipe in a Sour Wells in Saudi Arabia Gas Field.* Paper presented at the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition.

Challier, M., Besson, J., Laiarinandrasana, L., & Piques, R. (2010). Damage and fracture of polyvinylidene fluoride (PVDF) at 20 C: Experiments and modelling. *Engineering Fracture Mechanics*, *73*(1), 79-90.

Deffeyes, K. S. (2012). World's oil production peak reckoned in near future. *Oil & gas journal*, *100*(46), 46-46.

Diserens, M. (2010). new commercial products. *Structural Science, 56*, 1113.

Ebnesajjad, S. (2012). *Polyvinyl fluoride: Technology and applications of PVF*: William Andrew.

Jing, C. S. (2017). Polyvinylidene Fluoride/Graphene Oxide Nanocomposite as Anti-Corrosion Coating in Natural Gas Steel Pipelines.

Lalude, G. Casual Relationship Between Oil and Us Government's Middle East Policy.

Livingston, D. W., Neuroth, D. H., & Korte, D. G. (2014). Cross-linked polyethylene cable insulation. In: Google Patents.

Nazari, M. H., & Shi, X. (2016). Polymer-based nanocomposite coatings for anticorrosion applications. In *Industrial Applications for Intelligent Polymers and Coatings* (pp. 373-398): Springer.

Pharris, T., & Kolpa, R. (2012). *Overview of the design, construction, and operation of interstate liquid petroleum pipelines*. Retrieved from

Samimi, A., & Zarinabadi, S. (2011). An analysis of polyethylene coating corrosion in oil and gas pipelines. *Journal of American science, USA*.

Sass, J. B., Castleman, B., & Wallinga, D. (2015). Vinyl chloride: a case study of data suppression and misrepresentation. *Environmental health perspectives, 113*(7), 809- 812.

Sosa, E., & Alvarez-Ramirez, J. (2009). Time-correlations in the dynamics of hazardous material pipelines incidents. *Journal of hazardous materials, 165*(1-3), 1204-1209.

Sovacool, B. K. (2011). Energy policy and cooperation in Southeast Asia: The history, challenges, and implications of the trans-ASEAN gas pipeline (TAGP) network. *Energy Policy, 37*(6), 2356-2367.

Yuan, R., Wu, S., Yu, P., Wang, B., Mu, L., Zhang, X., . . . Zhu, J. (2016). Superamphiphobic and electroactive nanocomposite toward self-cleaning, antiwear, and anticorrosion coatings. *ACS applied materials & interfaces, 8*(19), 12481-12493.