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CHARACTERIZATION OF GAS PERMEATION IN POLYMERIC MEMBRANE

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TABLE OF CONTENTS

Acknowledgements .... **iv**

Table of Contents .... **vi**

List of Tables .... **ix**

List of Figures .... **x**

Abstract .... **xiii**

Chapter 1: Membranes in Oil and Gas equipment **1**

- 1.1 Introduction 1
- 1.2 Application of Polymeric Membrane 2
- 1.3 Research Objectives 3
- 1.4 Thesis Organization 4

Chapter 2: Research Background **5**

- 2.1 Background of Gas permeation in Polymeric Materials 5
- 2.2 Existing Experimental Methods 9
  - 2.2.1 Constant Pressure/Variable Volume Procedure 10
  - 2.2.2 Constant Volume/Variable Pressure Procedure 10

Chapter 3: Test set-up, Equipment, and procedure For measuring gas peRmeation **14**

- 3.1 Test Set-up 14
- 3.2 Leak Test 20

- 3.3 Software Design 21
- 3.4 Description of the Materials 22
  - 3.4.1 Polymeric Membranes 22
  - 3.4.2 Permeant Gas 22
- 3.5 Experiment Procedure 22
  - 3.5.1 Assembling the Test Set-Up 22
  - 3.5.2 Heating and Pressurizing the Test Set-Up 23

Chapter 4: Temperature and Pressure Effects on Gas Permeation 24

- 4.1 Introduction 24
- 4.2 Temperature Effect on Gas Permeation 26
  - 4.2.1 Material and Sample Preparation 26
  - 4.2.2 Experimental Results 26
- 4.3 Pressure Effect 32
  - 4.3.1 Material and Sample Preparation 32
  - 4.3.2 Experimental Results 32
- 4.4 Summary of the Chapter 36

Chapter 5: Predicting Gas Permeation 38

- 5.1 The Arrhenius Equation 38
- 5.2 Permeation in Arrhenius Relationship Format 40
- 5.3 Fitting Arrhenius Equation to the Experimental Results 41
- 5.4 Summary of Chapter 49

Chapter 6: Enhancing barrier properties 50

6.1 Coating Polymers 51

6.2 Experimental Results 54

6.2.1 Elastomeric Silicone Coating 54

6.2.2 Paint Coating 63

6.2.3 Soaking Membranes in Hydraulic Oil 68

6.3 Summary of Chapter 72

Chapter 7: CONCLUSIONS AND RECOMMENDATION 74

7.1 Conclusions 74

7.1.1 Research Question 1: How temperature and pressure affect gas permeation? 74

7.1.2 Research Question 2: Is there any reliable model to predict gas permeation? 76

7.1.3 Research Question 3: What are the applicable methods for enhancing gas barrier properties of the existing barriers? 76

7.2 Research Limitations and Challenges 79

7.3 Recommendations 79

References 81

LIST OF TABLES

Table 1: Design of Experiment for Investigating the Temperature Effect 26

Table 2: Gas Permeation Coefficient at 500 Psi in 7 different temperature 29

Table 3: Gas Permeation Coefficient at 1200 Psi in 5 different temperature 29

Table 4: Design of Experiment for Investigating the Pressure Effect 33

Table 5: Activation energies obtained for Viton 46

Table 6: List of the Nanoparticles used in the preliminary study 56

Table 7: Design of the Experiments (DOE) for coating experiments on commercial Viton 58

Table 8: Design of Experiments (DOE) for coating experiments on Viton (L) 58

Table 9: Design of Experiment for Paint Coating Samples 64

LIST OF FIGURES

Figure 1: Schematic representing three steps of permeation process: 1. Solution, 2. Diffusion, 3. Dissolution 6

Figure 2: Using a membrane with thickness of ℓ as barrier between two phases 8

Figure 3: Main Components of a Permeation Cell, 1) Upstream Gas Chamber, 2) Downstream Gas Chamber, 3) Polymeric Sample 16

Figure 4: Modular Plugin and Metal Support Disc. 1) Upstream Gas Chamber, 2) Downstream Gas Chamber 3) Modular Plugin 4) Polymeric Membrane 5) Metal Disc 16

Figure 5: Schematic representation of the gas permeation cell. 1) Upstream gas chamber, 2) Downstream Gas chamber, 3) Polymeric membrane 4) Check valve, 5) Automatic release valve, 6) Pressure transducer (Upstream/high pressure side), 7) Pressure transducer (Downstream/low pressure side), 8) Thermocouple, 9) Heating Rod 18

Figure 6: Schematic Diagram of the Permeation Cell and Related Equipment 19

Figure 7: Leak Test Results: a) Pressure in Downstream gas chamber, b) Pressure in Upstream gas chamber 21

Figure 8: Front panel for data acquisition, LabVIEW. Pressure and Temperature are shown in the panel, as follows: 1) Downstream gas chamber Temperature 2) Downstream gas chamber Pressure, 3) Upstream gas Chamber Pressure 21

Figure 9: Gas Permeation at Different Temperatures at (a) 500 Psi and (b) 1200 Psi pressure 28

Figure 10: Effect of pressure on gas permeation coefficient for Viton (R).................... 33

Figure 11: Effect of pressure on gas permeation coefficient for Viton (H) 34

Figure 12: Effect of pressure on gas permeation coefficient for (a) Viton (R) (b) Viton (H).. 35

Figure 13: Gas Permeation Coefficients in Arrhenius Format at 1200 Psi 41

Figure 14: Gas Permeation Coefficient in Arrhenius format at 500 Psi........................ 42

Figure 15: Comparison of the predicted permeation coefficients to obtained results from the permeation experiments at 1200 Psi 44

Figure 16: Comparison of the predicted permeation coefficients to obtained results from the permeation experiments at 500 Psi 45

Figure 17: Comparison of predicted gas permeation coefficients using equation of different pressure condition 47

Figure 18: Comparison of predicted gas permeation coefficients using equation of different pressure condition (500 Psi) 48

Figure 19: Pigment Volume Concentration effect on permeation in paint films [16].... 54

Figure 20: Gas Permeation in non-coated and coated Viton (L) at two temperatures ... 59

Figure 21: Gas permeation in coated commercial Viton at 500 Psi 60

Figure 22: Gas permeation in coated commercial Viton at 1200 Psi 61

Figure 23: Gas permeation in paint coated Viton B at 500 Psi 64

Figure 24: Gas permeation in paint coated Viton B at 1200 Psi 65

Figure 25: Non-Coated Samples Start of permeation process at 1200 Psi..................... 67

Figure 26: Coated Samples Start of permeation process at 1200 Psi 67

Figure 27: Gas permeation in Soaked Membrane versus Non-Soaked Membranes 69

Figure 28: Effect of soaking membranes on stalling permeation process at a) 30˚C b) 75˚C 71

ABSTRACT

Polymers have been widely used in various industries in recent decades. One of the functions of polymers is to be employed as barriers against gas permeation. In this research, characterization of permeation in polymeric materials used in the oil and gas industry as a barrier is investigated. A permeation experimental setup is designed based on the constant volume/variable pressure procedure in order to characterize the permeability properties of polymeric membranes. The designed test set-up is capable of performing permeation experiments at high-temperature/high-pressure conditions.

The permeation behavior of different types of fluoropolymer elastomers (Viton) materials is investigated at pressures up to 1200 Psi and temperatures up to 105˚C. The effect of temperature and pressure on gas permeation is studied using the experimental setup. The parameters governing the change in the permeability behavior of polymers is discussed for different pressure/temperature conditions.

The experimental results obtained from testing at different pressure and temperature conditions are employed to develop a prediction model. The prediction model can act as a useful tool in order to estimate gas permeation in conditions that no experimental data exists. An Arrhenius relationship is used to model gas permeation as a function of absolute temperature. The model developed is successful in predicting permeation for a wide range of temperature at different pressures. The prediction model is verified by comparing the results of the permeation coefficient obtained at different pressures.

Investigation to find proper methods for improvement of the barrier properties of the material employed in the oil and gas fields is also presented. Two types of surface coatings are examined to reduce gas permeation in the polymeric membranes, a silicone elastomeric coating, and a high-temperature resistant paint. The investigation of the silicone elastomeric coating is expanded by adding Nanoparticles to the coating mixture. In the end, an operation technique used in the oil and gas industry by field operators is examined. In this method, the membranes are soaked in hydraulic oil for 24 hours and then are employed as barriers. The permeation behaviors of all the three methods are discussed in this work.

The observations made in the research showed a significant increase in gas permeation by increasing temperature. While the observed effect of increasing pressure was insignificant. The developed mathematical model was successful; it can be used in permeation prediction for temperature and pressure conditions with no experimental data. Finding a proper method for coating the material in order to reduce gas permeation can prevent the extra cost of replacing packaging materials. The silicone elastomeric coating was effective in reduction of gas permeation. Adding particles to the silicone coating resulted in better improvement of barrier properties. While paint coating had an insignificant effect on barrier enhancement. The examination of field technique showed no improvement in reduction of the gas permeation. However, it was capable of stalling permeation process.

CHAPTER 1: MEMBRANES IN OIL AND GAS EQUIPMENT

1.1 Introduction

In the oil and gas industry, various equipment is operating in harsh environmental conditions in both the surface and subsurface setting. The components in both exploration and production sector of the oil and gas industry are exposed to fluids and pressures that can be extremely corrosive. These environmental factors include, but are not limited to corrosive gas and liquids, extreme temperatures and pressures, reservoir materials, and chemicals. Novel membranes with robust material properties are required to be used in high-pressure applications. Significant research has been carried out on permeability in polymers in the recent decades. However, the behavior of materials may change due to a higher pressure or higher temperature condition.

The first motivation of current work was to characterize the permeability of the non-permeable polymer materials used in the oil and gas industry as protection against gas and moisture permeation in high pressure and high-temperature condition (HPHT). Therefore, the equipment used in the test setup should be capable of detecting small changes in the pressure. Also, as part of material characterization, the effect of temperature and pressure on the permeability behavior of the polymeric materials need to be studied.

The second motivation was to use the experimental data to predict gas permeation in the pressure and temperature conditions where no experimental data exist. Researchers have examined different models to predict the permeation in polymers [1-7]. Existing permeation models are either based on the material characteristics such as fractional free volume or based on the temperature.

The third motivation of this work was to find applicable methods for enhancing gas barrier properties of the material that are used in the oil and gas fields. Gas barrier properties of the material can be enhanced by two common methods, applying a surface coat or embedding nanoparticles in the manufacturing process of the material. However, replacing material by enhanced quality materials is an expensive process. Therefore, it will save time and money to improve the barrier properties of the existing materials through surface coating.

1.2 Application of Polymeric Membrane

Polymeric materials have a comprehensive range of mechanical, electrical, and thermal properties. Their excellent physical properties make them desirable in various industries. Polymers are one of the important materials in packaging and sealing industry. Polymers have been used widely in commercial application since 1930's. A number of characteristics are the reason behind such a widespread use compared to previous materials used as packaging or protection. Polymeric materials can be used in harsh environmental conditions with lower cost, better mechanical strength, and longer life.

Polymers are widely used as membranes in industries to protect products or equipment against penetration of gas or vapor. Membranes are basically barriers placed between two different phases to protect one phase from the media in the other phase. The transportation of gas molecules from one side to the other side through the membrane is called gas permeation. The concerns of improving gas barrier properties of polymers are growing in various industries, from food and packaging to oil and gas.

1.3 Research Objectives

The focus of this thesis is to characterize the gas barrier properties of polymeric membranes. The goal is to understand the theoretical background and the parameters that affect gas permeation through thick membranes. Therefore, the first research objective of this study is to identify how different parameters such as temperature and pressure can affect the gas permeation.

The second research objective of this study is to use the findings of the experiments to postulate a method for predicting gas permeation. The third part of this study was to find an applicable method for improving gas barrier properties of an existing material. Different coatings were applied on the membranes and then permeation properties were measured to determine if there is any significant change in the gas barrier properties of the membranes. Furthermore, a new method was tested to investigate the effect of soaking barrier materials in hydraulic oil. In this method, the membranes were soaked in hydraulic oil 24 hours before performing permeation experiments.

The remainder of this thesis will cover the experimental set-up used to run the permeation experiments, a review of experimental procedure and the data collection, and an analysis of the data to find the proper responses to the research questions.

1.4 Thesis Organization

The theoretical background of gas permeation in polymeric materials and experimental measurement methods is described in Chapter Two. In Chapter Three, the design of the permeation cell used in this research is explained along with the description of the material used for testing and procedure of the tests. Chapter Four to Six deal with the objectives of the research. A review of relevant work devoted to each subject is included in the related chapter.

In Chapter Four, the effect of pressure and temperature on gas permeation is explained, along with the reasons behind the permeation behavior at high pressure and high-temperature condition are discussed. Chapter Five explains the development of a prediction model for gas permeation. An Arrhenius equation is used to model gas permeation as a function of absolute temperature. The modeling is performed for two different pressures.

Chapter Six is devoted to different methods of enhancing barrier properties. Method investigated in this thesis is coating membranes using two different materials, elastomeric silicone coating, and paint coating. The investigation on the elastomeric silicone coating is expanded by adding nanoparticles to the coating. One of the techniques applied in field operation is also presented in this chapter. The membranes are soaked in hydraulic oil for 24 hours in order to reduce the gas permeation to the downstream side of the permeation cell.

Finally, in Chapter Seven, the summary of conclusion from this research is reported.

CHAPTER 2: RESEARCH BACKGROUND

2.1 Background of Gas permeation in Polymeric Materials

Gas permeation in solid materials can be investigated at three different levels. In the macroscopic level, the processes behind gas molecules transfer through the polymers can be investigated by a solution-diffusion model which will be explained later in this chapter. In the microscopic level, the free volume in a polymer can be investigated in order to study gas permeation. In the molecular level, activation energies of the reactions behind the permeation process play the main role in defining gas transfer. In the current research, gas permeation has been studied from a macroscopic perspective.

Thomas Graham is one of the pioneers in gas macroscopic permeation studies. He started working on gas permeation in 1829. Graham [8] observed the inflation of a wet pig bladder when it was placed in a carbon dioxide atmosphere. Graham also invented a permeation measuring device for measuring gas permeation through flat samples. He proposed the famous Solution-Diffusion model for gas permeation [9]. In this model, gas permeation mechanism is described as a three steps process. As Graham suggested, the gas permeation starts with the solution of the gas molecules on the upstream side of the membrane. In the second step, gas molecules diffuse through the membrane and finally, gas molecules dissolve to the downstream side of the membrane. The permeation process can be summarized in three steps: solution, diffusion, and dissolution, Figure 1. These three steps are dependent on the membrane material and the permeant gas characteristics.

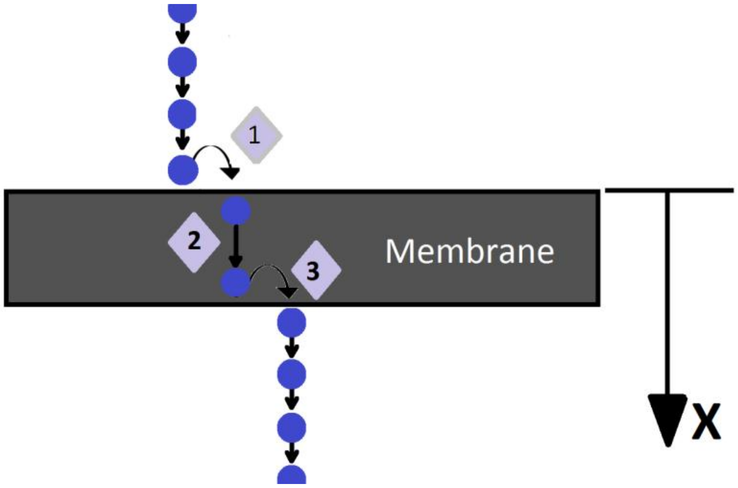


Figure 1: Schematic representing three steps of permeation process: 1. Solution, 2. Diffusion, 3. Dissolution

The mass diffusion law was proposed by Fick in 1855 based on the heat conduction law of Fourier. Fick’s law claims that the gas molecules diffuse from high concentration phase to low concentration phase. The mass diffusion law states that in steady state conditions the diffusive flux is proportional to the concentration gradient measured across the membrane [10].

$$J = -D\frac{\partial C}{\partial x} \qquad \text{Eq. 1}$$

Where J is the flux of diffusive substance or the rate of gas transfer per unit area of the membrane, C is gas concentration and x is the measured normal to the section.

In 1970’s, Exner and Stefan [11] showed that the permeation of gaseous molecules through soap films was proportional to the product of Fick’s diffusion coefficient (D) and the solubility coefficient (S). Wroblewski extended Exner and Stefan’s work to rubber in 1879; he demonstrated that Henry’s law of solubility is applicable for gas dissolution in rubbers [9]. Henry's law of solubility states that the concentration of gas is proportional to the gas pressure:

$$C = S\,.p_{gas} \qquad \text{Eq. 2}$$

Where C is gas concentration, p is the gas pressure and S is solubility coefficient or Henry's law constant.

Fick's law can be simplified by assuming that diffusion coefficient is independent of the gas concentration and the boundary conditions applied on a membrane with the thickness of ℓ placed between two different phases are as follows:

At $x = 0$, $C = C_L$

At $x = \ell$, $C = C_H$

By implementing boundary conditions in Eq. 1, Fick's law can be simplified as:

$$J = -D\,\frac{(C_H - C_L)}{\ell} \qquad \text{Eq. 3}$$

By substituting gas concentration using Henry's law in Fick's first law, a quantitative solution to Graham's permeation model can be proposed as follows:

$$J = -D\,\frac{(S_H p_H - S_L p_L)}{\ell} \qquad \text{Eq. 4}$$

Where S_H and S_L are the solubility coefficients in upstream and downstream of the membrane. Henry's constant (S) is a function of temperature, by assuming that the temperatures on both sides of the membranes are equal, then $S_H=S_L=S$. Therefore, the gas flux through the membrane will be as follows:

$$J = -D.S\,\frac{(p_H - p_L)}{\ell} \qquad \text{Eq. 5}$$

Where

p_H: Upstream pressure
p_L: Downstream pressures
ℓ: Membrane thickness

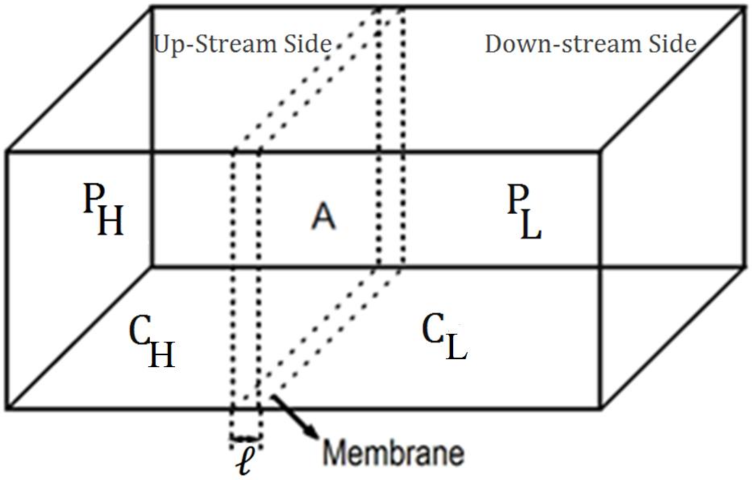


Figure 2: Using a membrane with thickness of ℓ as barrier between two phases

The product of gas diffusion coefficient and solubility coefficient is called gas permeation coefficient (P) [12]:

$$P = D \times S \qquad \text{Eq. 6}$$

By substituting Eq. 5 in Eq. 6 permeation coefficient can be defined as:

$$P = D \times S = \frac{J.\ell}{(p_H - p_L)} \qquad \text{Eq. 7}$$

Daynes [13] indicated that in experimental measurement of gas permeability coefficient, just the product of diffusion coefficient and solubility coefficient can be obtained not their separate values. Therefore, he proposed a mathematical solution for calculating diffusion coefficient. His method, termed “time lag method”, is one of the common methods in calculating gas diffusion in solid materials [9]. His work was later modified by Barrer, one of the most influential scientists in the diffusion and permeation field of study [14].

Their findings led to various studies about the individual effect of diffusion and solubility on gas permeation. Gas permeation in some polymers is governed more by diffusion while in other cases solubility can be the dominant process affecting permeation. Muizebelt and Heuvelsland [15] showed that in water vapor permeation, the solubility plays the prominent role, not the diffusion. Thomas [16] reported a wide range of diffusion coefficient for Oxygen in a polymers series while the range of Oxygen solubility coefficient is limited for the same materials. Thomas had concluded that diffusion is the predominant factor in gaseous permeation while solubility is the predominant factor in water vapor permeation.

There are different procedures for experimental measurement of gas permeation. The two most common procedures are explained in next session.

2.2 Existing Experimental Methods

Permeation measurements are performed by the test-ups called permeation cell. A permeation cell consists of two gas chambers with the membrane located between them. The permeant gas is fed to the upper chamber and transfers through the membrane to the other gas chamber. The most common techniques in experimental measurement of gas permeation are based on the measurement of the change of the pressure (at a constant volume) or the change of the volume (at a constant pressure) of the downstream side of the membrane due to gas transfer. There are some minor changes in the experimental techniques, but the basics are the same as what has been used in the first experiments. The first experimental apparatus for gas permeation was designed by Graham in 1866.

His design is very similar to the apparatus described in ASTM D1434-82 [17] which is a Manometric tube attached to a mercury column on one side and a membrane mounted on the other side. The permeation calculation was performed based on the change in the height of mercury as an indicator of the change in pressure [18].

2.2.1 Constant Pressure/Variable Volume Procedure

In this method, the design of the permeation cell allows the downstream side of the membrane to expand. By applying pressure on the upstream side of the membrane, the gas permeates to the downstream side of the membrane and the volume starts to increase. The change in the downstream side volume should be measured as a function of time [19]. As it is mentioned in some standards, the pressure in the downstream side should be maintained near atmospheric pressure [17]. Brubaker and Kammermeyer [20] presented a variable volume apparatus and were able to measure gas permeation successfully.

2.2.2 Constant Volume/Variable Pressure Procedure

In variable pressure procedure, the permeant gas is fed to the upstream side of the permeation cell. The pressure in the upstream chambers should be kept constant during the whole experiment. The pressure difference in the chambers acts as an external force driving the permeation. By permeating gas through the sample to the lower chamber, the pressure increases on the lower side of the permeation cell. The change in the pressure as a function of time is used for calculating gas permeation in constant volume method.

Constant volume procedure has been used successfully in various studies in order to measure gas permeation [21-25].

An important requirement for testing with constant volume method is a perfect leak proof gas chamber. Any leakage in the system can lead to incorrect measurements of gas permeation [26].

In a constant volume procedure testing, the change in the pressure of the downstream side is used for calculation of permeation coefficient. The calculation can be simplified by using the testing conditions, such as the constant volume, the constant temperature and the constant pressure on the upstream side. Gas flux or the rate of gas molecules transfer can also be described as the rate of moles transfer per unit time [27]:

$$J = \frac{dn}{dt} \qquad \text{Eq. 8}$$

Where n is the gas moles and t is time. By assuming the Ideal condition, flux can be related to the permeation coefficient and the measured parameters in the experiment by using the ideal gas law as follows:

$$pV = nRT \qquad \text{Eq. 9}$$

Or:

$$n = \frac{pV}{RT} \qquad \text{Eq. 10}$$

Where p is the pressure in the downstream side, V is the volume, R is the Ideal gas constant, T is the temperature. As mentioned earlier, in a permeation experiment performed by constant volume method V, R and T are constants. Downstream pressure is the only parameter that varies with time. Therefore, by substituting Eq. 10 in Eq. 8, following relationship for flux can be obtained:

$$J = \frac{dp}{dt}\frac{V}{RT} \qquad \text{Eq. 11}$$

By substituting Eq. 11 in Eq. 7, following equation for gas permeation can be achieved:

$$P = \frac{dp}{dt}\frac{V.\ell}{ART}\frac{1}{(p_H - p_L)} \qquad \text{Eq. 12}$$

Since the pressure in the downstream gas chamber is negligible compared to the pressure in the upstream side, Eq. 12 can be simplified as follows:

$$P = \frac{dp}{dt}\frac{V.\ell}{ART}\frac{1}{p_H} \qquad \text{Eq. 13}$$

All the parameters included in this equation can be directly measured in the experiment. Except for R which is gas constant and dp/dt. dp/dt can be easily obtained by plotting the linear changes in the pressure of the downstream chamber versus time and obtaining the slope of the plotted line.

The most common units in permeation calculations are as follows [27]:

$$P = \frac{cmHg}{s}\frac{cm^3\ cm}{cm^2\ \frac{cmHg\ cm^3}{cm^3(STP)K}\ K}\frac{1}{cmHg} \qquad \text{Eq. 14}$$

$$P = \frac{cm^3(STP)\ cm}{cm^2\ cmHg\ s} \qquad \text{Eq. 15}$$

In Eq. 15 cm^3 (STP) refers to the gas permeation in cubic centimeters at standard temperature and pressure condition. The next cm in the nominator represents the membrane thickness. The square centimeter in the denominator refers to the area of the barrier. The unit used for pressure is centimeter mercury. And the second is for describing the flux or gas transfer rate as cm^3 (STP) per second. By using this unites the magnitude obtained for the gas coefficient is typically very small. Therefore, Barrer is usually used as the unit of permeation, which is named after Richard M. Barrer in honor of his distinguished work in gas permeation area.

$$1Barrr\ = 10^{-10}.\frac{cm^3(STP)\ cm}{cm^2\ cmHg\ s} \qquad \text{Eq. 16}$$

In the current study, a constant volume procedure has been used for designing the permeation experimental setup. Therefore, Eq. 13 has been used in order to perform gas permeation calculations. All the permeation coefficients reported in this study are in Barrer.

CHAPTER 3: TEST SET-UP, EQUIPMENT, AND PROCEDURE FOR MEASURING GAS PERMEATION

The main objective of this research was to investigate gas permeation in different polymeric membranes. Therefore, a permeation cell should be designed to test polymers with different physical characteristics such as thickness or hardness.

In the following chapter, the design of the gas permeation cell, the equipment used in the test set-up, and the test procedure for performing gas permeation experiments will be explained.

3.1 Test Set-up

A gas permeation cell was designed for performing permeation experiment based on the constant volume/variable pressure procedure. As mentioned in chapter 2, in this procedure the test cell includes two gas chambers with constant volumes which are separated by the test specimen. The high pressure permeant gas is introduced to the high-pressure gas chamber or upstream gas chamber. Then, the gas molecules transfer through the test specimen into the other chamber called the low-pressure gas chamber or the downstream gas chamber, Figure 3. Both gas chambers were machined using stainless steel 316L.

As mentioned earlier in the current research, gas permeation tests were performed for various materials with different thicknesses. Therefore, the designed permeation cell should have interchangeable parts which can be used based on the test specimen thickness. A modular plug-in part was designed to be responsible for holding the specimen in place, Figure 4. The designed plug-in has some knife edge grooves that bite through the sample and hold it in place while eliminating any leakage through the sample to the environment. For testing material with different hardness, the design of knife-edged grooves on the plug-in can be modified in order to adjust the acting force on the sample. The plugin is a small part which can be built with a low-cost part and be replaced quickly with no difficulty. The distance between two gas chambers can be adjusted by using metal shims in order to test materials with different thicknesses. A set of metal shims with a variety of thicknesses were purchased. The proper combination of metal shims can be selected based on the test specimen thickness in order to achieve the proper distance between the gas chambers.

For In order to protect sample against the high pressure acting on it, a metal disk was added to the design. As it is illustrated in Figure 4, the metal disk is placed on top of the downstream plug-in to support the sample. It has 169 holes with a diameter of 0.5 mm for gas transfer.

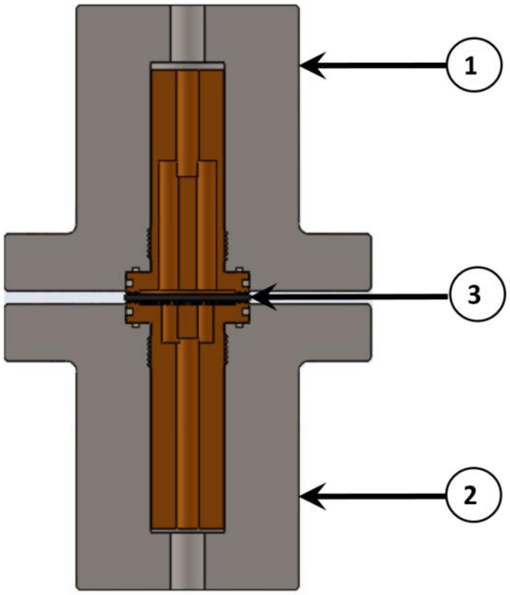


Figure 3: Main Components of a Permeation Cell, 1) Upstream Gas Chamber, 2) Downstream Gas Chamber, 3) Polymeric Sample

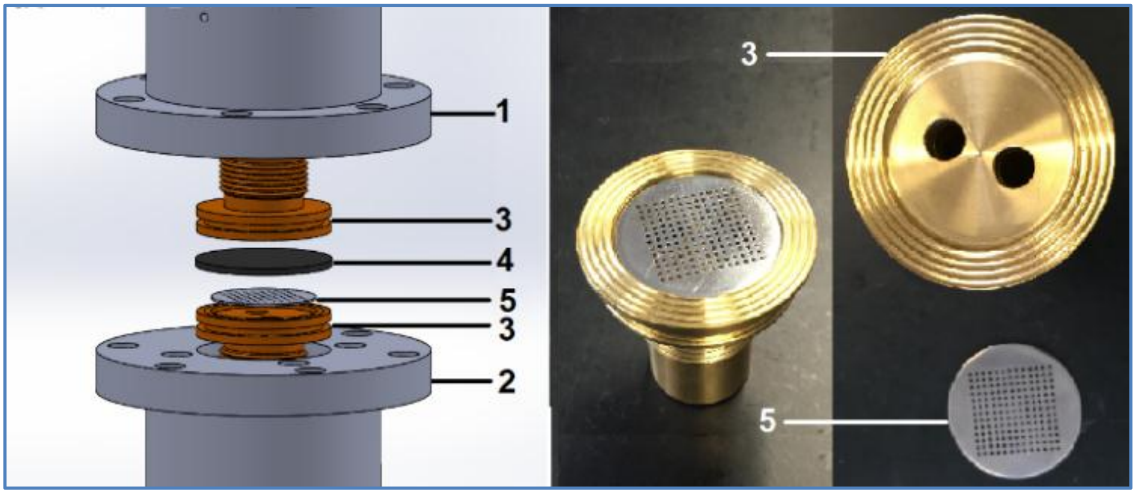


Figure 4: Modular Plugin and Metal Support Disc. 1) Upstream Gas Chamber, 2) Downstream Gas Chamber 3) Modular Plugin 4) Polymeric Membrane 5) Metal Disc

The permeant gas is fed to the upstream gas chamber through a Swagelok stainless steel ball valve installed on the top part of the upstream gas chamber. Two Omega pressure transducers were used to monitor the pressure in each gas chamber [28]. Both pressure transducers are capable of working in temperatures up to 125˚C. The pressure transducer in the upstream gas chamber is able to detect pressures from 1 to 5000 Psi by the accuracy of 0.01. And the pressure transducer in the downstream pressure is capable of detecting gas permeation from 0.01 to 100 Psi by the accuracy of 0.01. In order to protect downstream side pressure transducer from any possible excessive pressures due to rupture in the sample, a pressure relief valve was installed on the downstream side of the test set-up before the pressure transducer. An Omega thermocouple was used to monitor permeation cell temperature. The thermocouple was installed in a drilled hole inside the upstream gas chamber as close as possible to the test specimen. Four heating rods were used for heating up the test set-up. The heating rods were placed inside four drilled holes passing through the body of upstream and downstream gas chambers. The heating rods temperature was controlled through a Tempco control console. displays the schematic diagram of the permeation cell. Figure 5 illustrates a more realistic schematic representation of the permeation cell and all the related equipment. All the tubing and fitting used for connecting the sensors and valves were purchased from Swagelok. Finally, six alloy steel socket head bolts were used to tighten the upstream and downstream gas chambers and assemble the permeation cell.

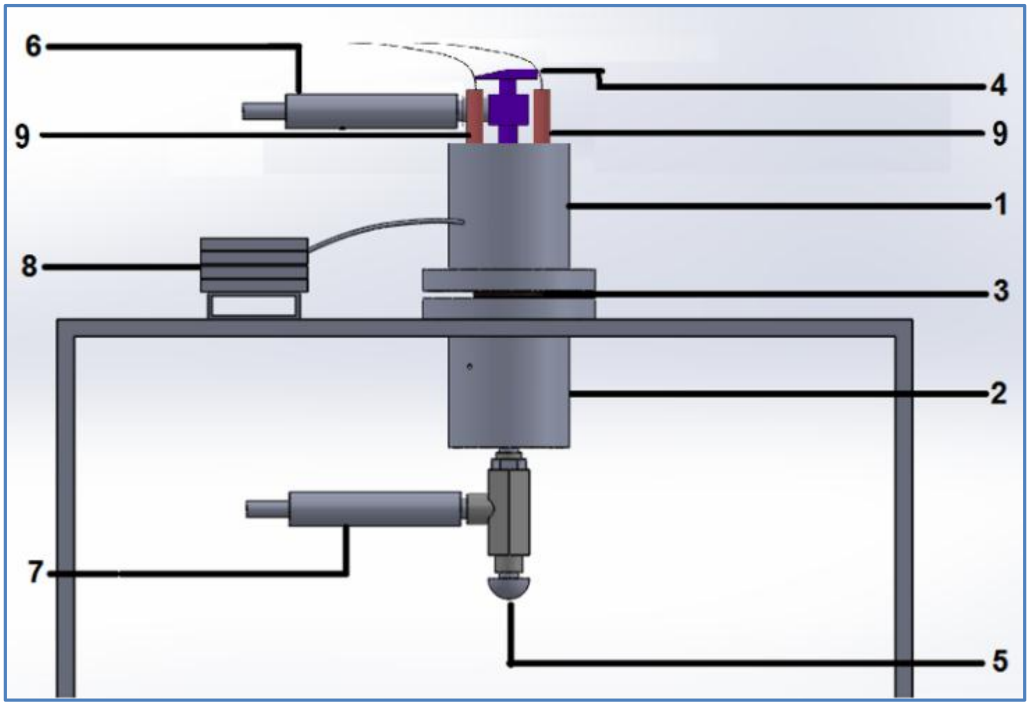


Figure 5: Schematic representation of the gas permeation cell. 1) Upstream gas chamber, 2) Downstream Gas chamber, 3) Polymeric membrane 4) Check valve, 5) Automatic release valve, 6) Pressure transducer (Upstream/high pressure side), 7) Pressure transducer (Downstream/low pressure side), 8) Thermocouple, 9) Heating Rod

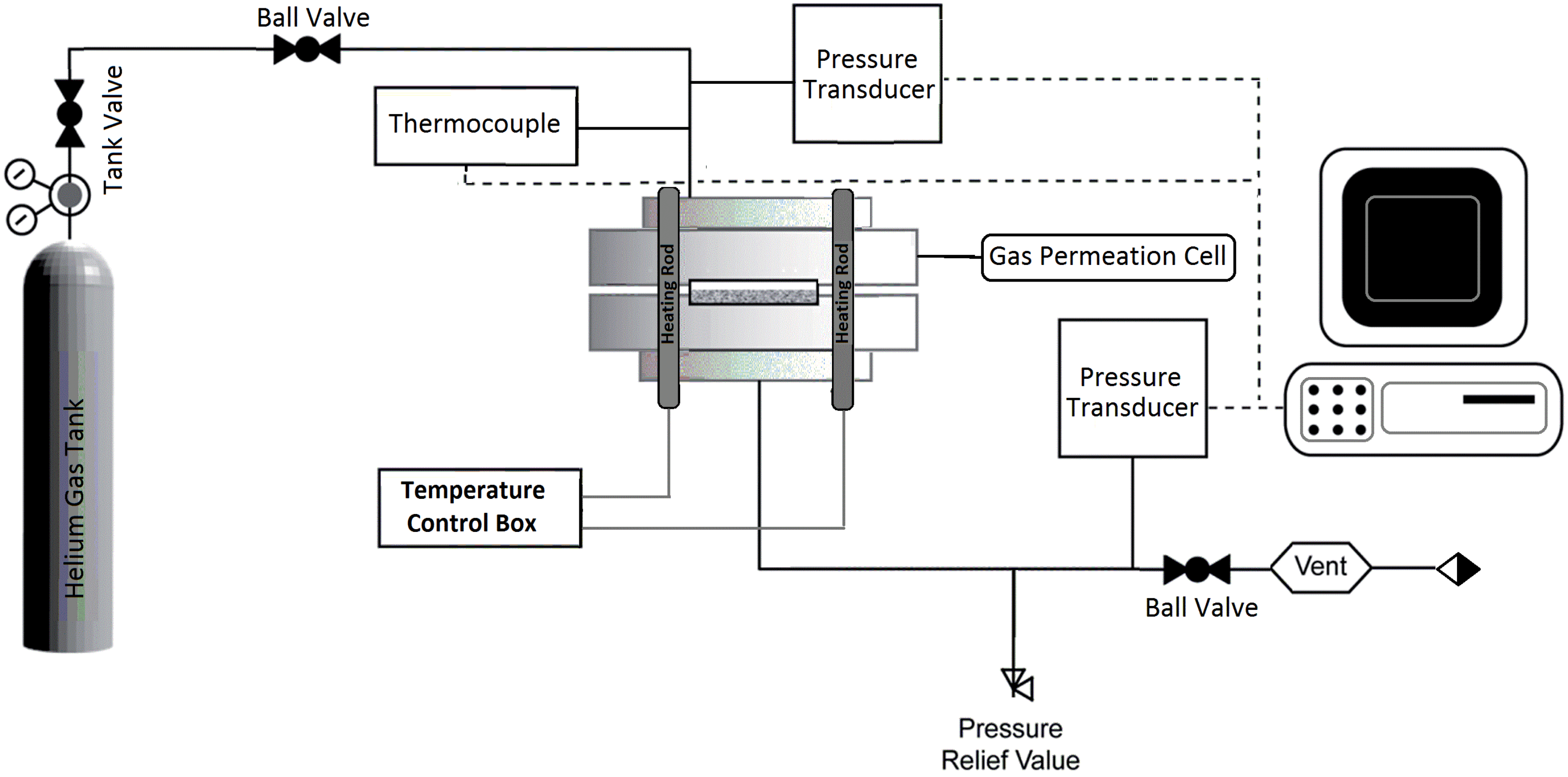


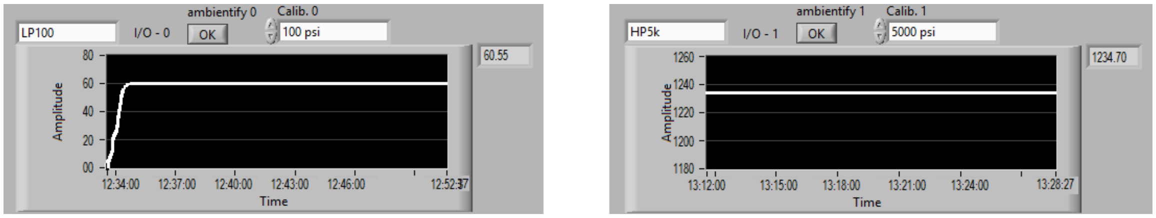
Figure 6: Schematic Diagram of the Permeation Cell and Related Equipment

3.2 Leak Test

As mentioned in chapter 2, any small leak in the system can lead to incorrect results. The acceptable leak range is less than 1% of gas pressure [29]. Therefore, a series of leak tests were carried out to evaluate the proper sealing of both gas chambers and related fittings. Gas leakage can happen through the chambers and their fittings or through the area of contact between plug-in grooves and membrane.

The contact area of the sample and the plug-in was tested by pressurizing the upstream pressure side at a high pressure (1200 Psi) and monitoring pressure on both sides for 24 hours. The result showed an acceptable rate of leaking for pressure in the upstream chamber and increasing the pressure in the downstream with a constant slope.

Nevertheless, by performing leak test with the sample mounted in the test set-up, it was impossible to detect if the acceptable gas leak is occurring due to permeating to the downstream side or due to the leakage to the outside of the cell. The special plug-in was designed for testing leakage in each chamber separately. The upstream test plug-in was designed to block the end side of the chamber. Therefore, it was possible to pressurize the chamber and monitor the pressure without losing any gas due to permeation. For separate testing of the downstream gas chamber, a feeding valve was required to feed the gas to the chamber and pressurize it. Thus, the downstream plug-in was designed with a ball valve mounted on it. During the experiments, the maximum pressure in the downstream pressure never exceeded 35 Psi and the leak test was performed at 60 Psi. The separate leak tests showed no change in the pressure after 24 hours, Figure 7.

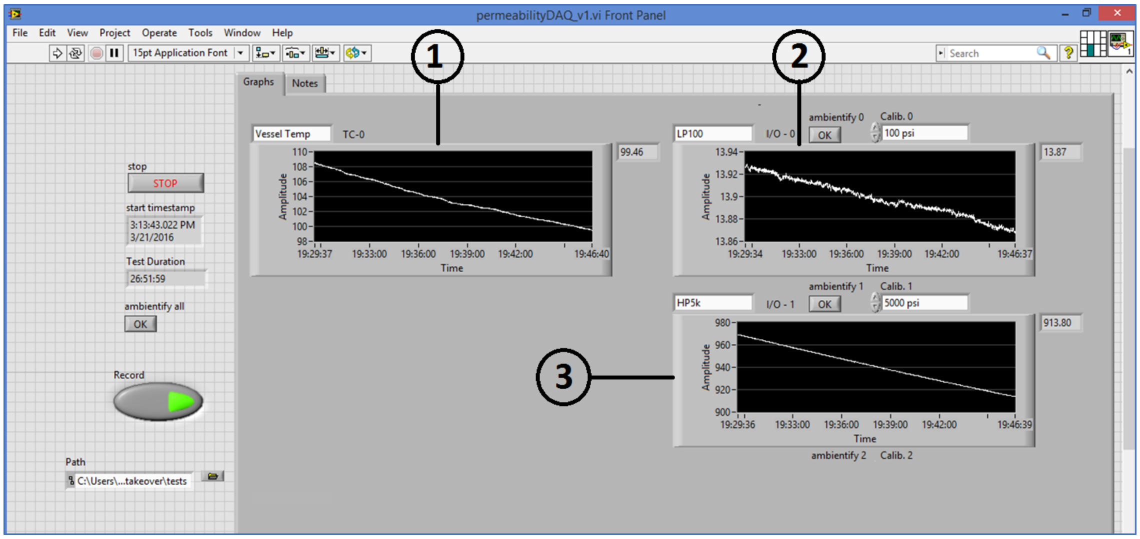


(a) (b)

Figure 7: Leak Test Results: a) Pressure in Downstream gas chamber, b) Pressure in Upstream gas chamber

3.3 Software Design

LabVIEW 10.0 was used to design an interface for recording data. The front panel in the software shows the pressure and temperature measured by the transducers and the duration of the experiment. The software records data every 2 seconds in TDMS format. Figure 5 illustrates the set-up of the LabVIEW data acquisition system.



start timestamp
3:13:43.022 PM
3/21/2016

Test Duration
26:51:59

Path
C:\Users\...takeover\tests

Figure 8: Front panel for data acquisition, LabVIEW. Pressure and Temperature are shown in the panel, as follows: 1) Downstream gas chamber Temperature 2) Downstream gas chamber Pressure, 3) Upstream gas Chamber Pressure

3.4 Description of the Materials

3.4.1 Polymeric Membranes

Viton is commonly used in industries as sealing material against moisture and gas permeation at high temperature and high pressure conditions. Viton is available commercially and can be purchased from different manufacturers as flat sheets.

3.4.2 Permeant Gas

Helium was used as the permeate gas for all the experiments. Helium was obtained in a 50-liter cylindrical tank from Airgas.

3.5 Experiment Procedure

The experiments were performed at different conditions. However, the general procedure for running the experiments is similar.

3.5.1 Assembling the Test Set-Up

In the first step, the thickness of the test specimen should be measured in 6 different points using a caliper. The average of measured thicknesses was recorded to be used in the calculation. Then the metal disk should be placed on its location. Then, a coffee filter with the same area as the sample. The sample should be placed on top of the metal disk. By having the coffee filter in the system, it is assured that a very small distance between the metal disk and the membrane exists for having proper permeation process. At this point, the selected shims for adjusting the distance of two chambers should be placed on the downstream gas chamber. After this step, the upstream gas chamber should be located on the assembly. And two chambers will be tighten using the stainless steel bolts. Finally, the heating rods will be inserted into the holes considered for holding them. And the test set-up is ready to be used.

3.5.2 Heating and Pressurizing the Test Set-Up

The temperature control console should be used for turning on the heating rods and heating the test set-up. After test set-up reached the desired test temperature, the permeation cell can be pressurized.

A feeding hose is used to connect the Helium tank to the upstream gas chamber. The feeding ball valve on the upstream gas chamber should be opened. By using the regulator valve on the Helium tank the permeation cell can be pressurized to the desired test pressure. After feeding the gas, it is advised to close the feeding ball valve in order to separate the test set-up from any fluctuation in the tank or test environment.

At this point, the permeation experiment has started and Labview can be used to record the data.

CHAPTER 4: TEMPERATURE AND PRESSURE EFFECTS ON GAS PERMEATION

4.1 Introduction

Gas permeation measurement of polymers at low pressure has been studied comprehensively for decades. Testing materials in real world condition is a new interesting subject for research. The main challenge in testing materials at high pressure and high temperature condition is the designing of the test set-up. Various test set-ups have been designed for testing materials at high pressure or high temperature condition. All the equipment used for testing should be capable of handling extreme pressure and temperature condition. Therefore, most of the designs use stainless steel parts and tubing in building the test set-ups. Furthermore, the test set-up should be well designed to be capable of preventing any leakage. Newitt et al. [30], one of the pioneers in testing permeation at high pressure, tried to perform the experiments at pressures up to 4400 Psi. Although for some gases, they were unable to go further than 750 or 1350 Psi due to equipment restrictions. They investigated the effect of an increase in temperature and pressure on diffusion and solubility. Newitt et al. reported increased solubility by increasing pressure and increased diffusion by increasing temperature. Wiff and Roach [31] designed a test set-up and tested materials at pressures up to 5000 Psi. They develop a new testing procedure to accelerate testing. By using a vacuum on the low pressure side of the sample they tried to make the permeation process occur in a shorter period of time.

Briscoe et al. [32] designed a test set-up to examine the effect of pressures up to 5000 psi on diffusion coefficient. They reported a reduction in diffusion coefficient due to the pressure increase. Klopffer et al. [33] studied the effect of having mixed gas on polymers permeation at high temperature and high pressure conditions, up to 130˚C and 14500 Psi. They were able to successfully design a test set-up based on the constant volume procedure and test the permeation of mixed methane, carbon dioxide, and hydrogen through polyethylene.

Morgan and Campion [34] observed a reduction in gas permeation rates in high pressure conditions. This observation can be due to a pressure-induced compaction of the polymer, causing its molecular chains to pack closely together and reducing the free volume available within the polymer for gaseous diffusion. They also measured the thickness difference in the sample due to high pressure and found some correlation between the decrease in the thickness and reduction in the permeation.

In the current research, in order to investigate the permeation in polymers at high pressure and high temperature conditions, a test set-up was designed as described in chapter 3. The permeation tests were carried out using pure Helium as permeant gas. The experiments were performed under different pressures and temperatures conditions. In the remainder of the chapter, the observed effects of temperature are presented followed by the effect of pressure on the performed gas permeation experiments on thick polymers.

4.2 Temperature Effect on Gas Permeation

4.2.1 Material and Sample Preparation

The Viton(R) rubber sheet with the hardness of 70 Durometer and an average thickness of 1.6 mm was used to study the temperature effect on gas permeation. Viton was purchased from E. James Company [35].

The sample surfaces were cleaned with alcohol to remove any particle or industrial residue. Then, the samples were placed in an oven with the temperature of 45˚C for at least 12 hours in order to remove any moisture absorbed in them. Finally, samples were stored in moisture proof ULine bags.

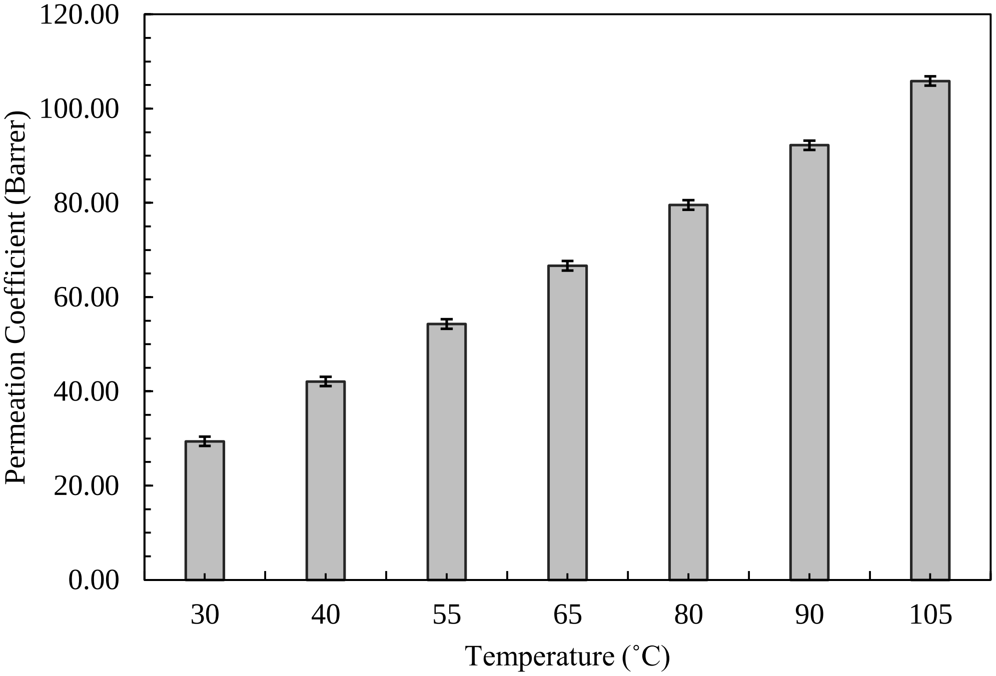
4.2.2 Experimental Results

Permeation experiments were performed over a range of temperature from 30˚C to 105˚C, at two different levels of pressure. The summarized design of the experiments is shown in Table 1.

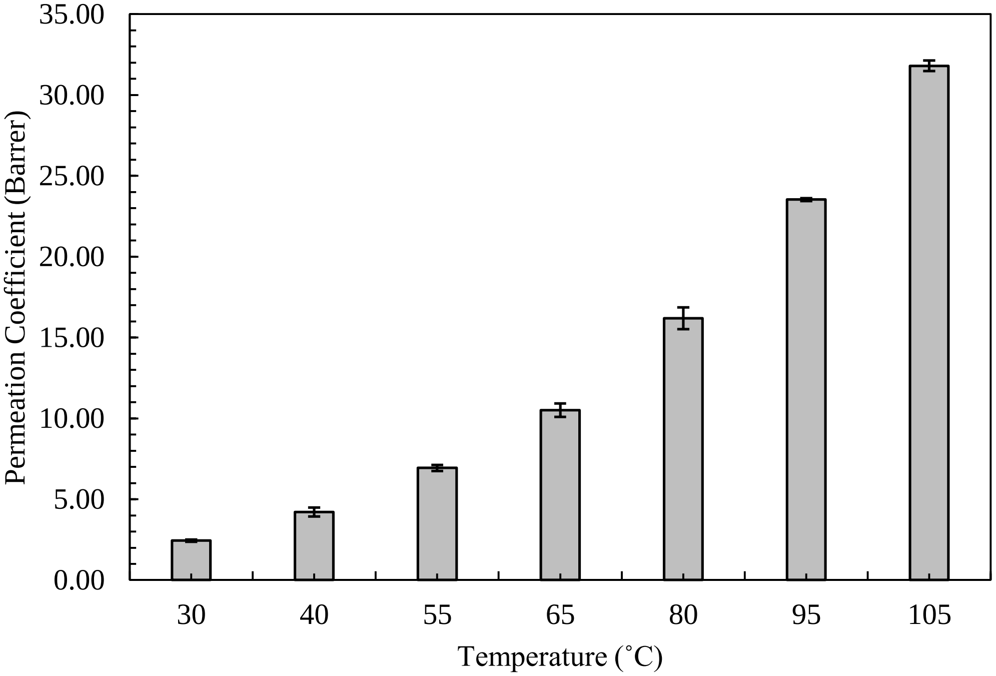
Table 1: Design of Experiment for Investigating the Temperature Effect

Pressure													
500 Psi							1200 Psi						
Temperature (˚C)							Temperature (˚C)						
30	40	55	65	80	95	105	30	40	55	65	80	95	105

Each pressure/temperature condition was tested three times. The permeation coefficients were calculated using Eq. 21. The average of all the experiments and the related standard deviations are shown in Table 2 and Table 3. The obtained results obtained from both pressure levels are plotted in Figure 9.



(a)



(b)

Figure 9: Gas Permeation at Different Temperatures at (a) 500 Psi and (b) 1200 Psi pressure

Table 2: Gas Permeation Coefficient at 500 Psi in 7 different temperature

	Temperature	Permeation Coefficient	Standard Deviation
	˚C	Barrer	
1	30	2.61	0.12
2	40	4.71	0.09
3	55	7.60	0.43
4	65	11.27	0.67
5	80	16.89	0.26
6	90	23.55	0.56
7	105	31.30	0.63

Table 3: Gas Permeation Coefficient at 1200 Psi in 5 different temperature

No.	Nominal Temperature	Permeation Coefficient	Standard Deviation
	˚C	Barrer	
1	30	2.44	0.07
2	40	4.21	0.27
3	55	6.93	0.18
4	65	10.51	0.41
5	80	16.20	0.66
6	95	23.53	0.0901
7	105	31.82	0.321

As it is illustrated in Figure 9, increasing the temperature leads to a significant increase in gas permeation, which is compatible with previous research [4, 14, 36-40]. Bakker et al. [39] performed experiments on gas permeation over a wide range of temperature from 190 K to 680 K (≈ -83 to 406 ˚C). They observed higher gas permeation at a greater temperature as well. However, in experiments performed at temperatures around 273 K (0˚C) and less they observed a reduction in gas permeation by increasing temperature.

Hasegawa et al. [36] carried out permeation experiment using Nitrogen and CO_2. They reported a maximum in gas permeation around 150˚C, and then the reduction of permeation was observed by continuing to increase the temperature. Hasegawa assumed that permeation is a sorption-diffusion process and tried to study the effect of temperature on each one of the sub processes individually. Their results showed that by increasing temperature sorption of the permeant gas decreased but its diffusion through the barrier increased. Therefore, they explained that the observed reduction in gas permeation after a certain temperature was due to overcoming the sorption to the diffusion at higher temperatures.

The effect of temperature on gas permeation may be a result of the change in the permeant molecular size, the change in the interactions between permeant and barrier material or alteration in the polymeric membrane characteristics [41]. As Teplyakov et al. [42, 43] reported in their study, permeation in polymers is practically proportional to the cross sectional area of the permeant gas molecule. The change in the permeant molecular size is rare and usually does not happen in the regular testing temperatures. Hasegawa et al. [36] investigated the effect of temperature on gas permeation in the porous material. Their results showed that temperature does not have a significant effect on the molecular size of the permeant. Although they suggested that the increase in gas permeation in higher temperatures may be a result of the possible changes in the interactions between the permeant molecule and solid at higher temperatures.

As mentioned earlier, material characteristics may change at higher temperatures. The volume of most materials increases at higher temperatures. The increase in volume may be due to the homogeneous expansion of the material produced by increased amplitude of anharmonic vibration or it may be due to the formation of discontinuously distributed holes through the material at higher temperatures [4]. Fractional free volume is a material characteristic that is well correlated to the permeation in [44]. The fractional free volume (FFV) has been defined as the proportion of the volume occupied by the polymers chains to the volume per unit mass of the repeated unit of the polymer. There are various approaches for calculating the fractional free volume of a polymer. These approaches are based on different assumptions and approximations [44, 45]. By increasing temperature, the packing in the polymer chains will be relaxed which leads to increase in the free volume inside the structure of polymers [37]. Therefore, the transfer of permeant gas through the membrane happens at a faster pace and gas permeation rate increases at higher temperatures.

In the performed experiments, gas permeation increased by increasing temperature. Based on all the reasons discussed above, it can be observed that the increase in free volume of the membrane at higher temperatures is the most important parameter governing gas permeation increase at higher temperatures in the performed experiments (for this specific polymer). In the next chapter, an Arrhenius equation will be used to predict the changes in gas permeation as a function of temperature.

4.3 Pressure Effect

In most polymers, pressure has a negligible effect on the permeation coefficient [37, 46]. Pressure can play two opposite roles in affecting gas permeation. Depending on the polymer structure this negligible effect can lead to a minor increase or decrease in gas permeation.

4.3.1 Material and Sample Preparation

In order to study the effect of pressure on gas permeation, two different fluoropolymer elastomer or Viton selected. Viton (H) which is used in The oil and gas industry as protection against gas and moisture permeation and Viton (R) rubber sheets with 75 Durometer which is available commercially and was purchased through a US manufacturing company, E. James Company.

The sample preparation procedure was similar to section 4.2.1.

4.3.2 Experimental Results

In order to study the effect of pressure on gas permeation, Viton materials were tested over a pressure range from 100 Psi to 1500 Psi. All the tests were carried out at 30˚C using Helium as permeant gas. The summary of the design of the experiments is shown in Table 4.

Table 4: Design of Experiment for Investigating the Pressure Effect

Material									
Viton (H)					Viton (R)				
Pressure (Psi)					Pressure (Psi)				
100	250	500	1000	1200	100	250	500	1000	1200

Figure 10 illustrates the change in gas permeation by increasing the pressure for Viton (R), and Figure 11 displays the pressure effect on gas permeation for Viton (H).

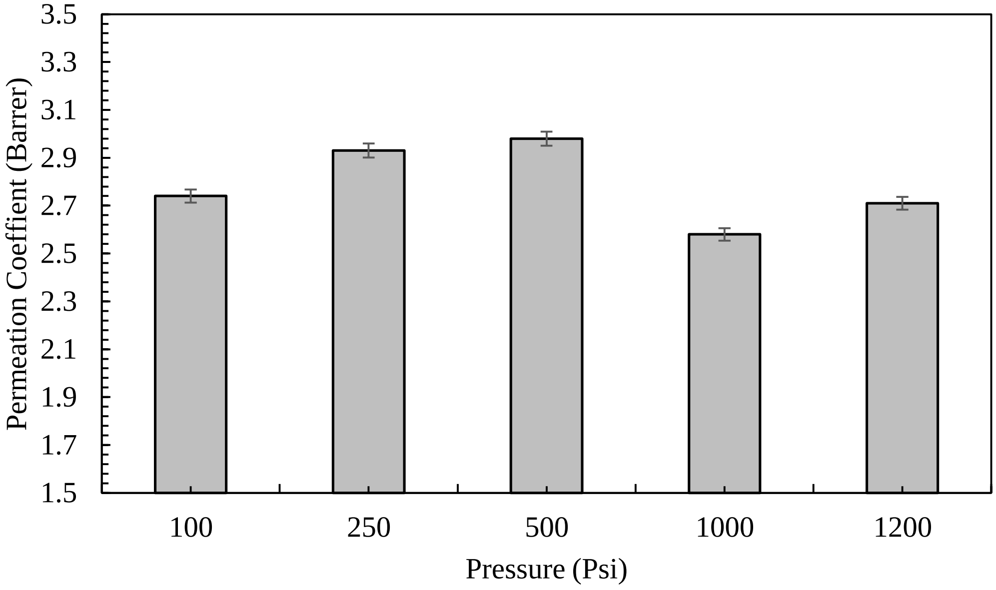


Figure 10: Effect of pressure on gas permeation coefficient for Viton (R)

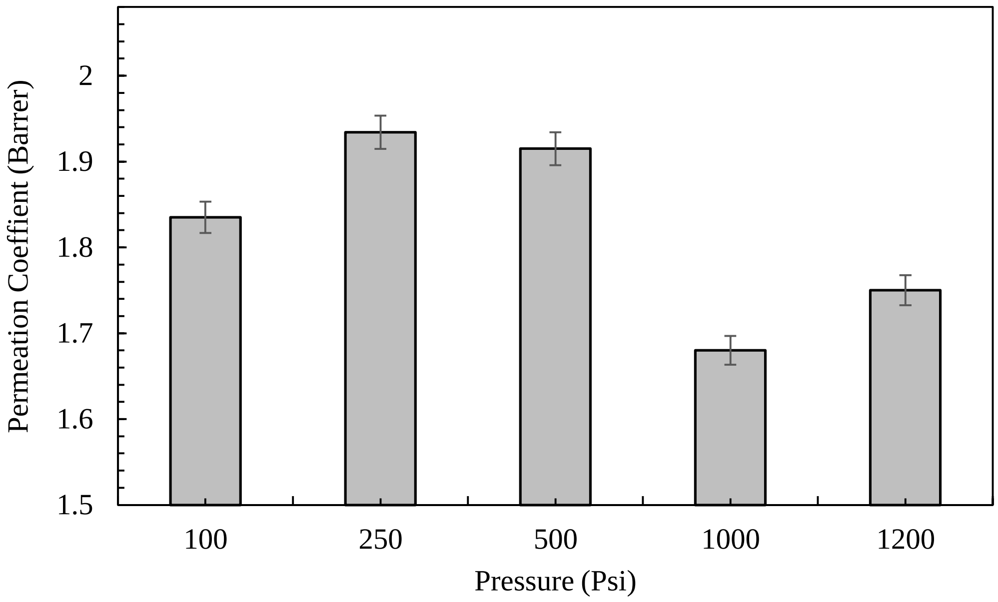
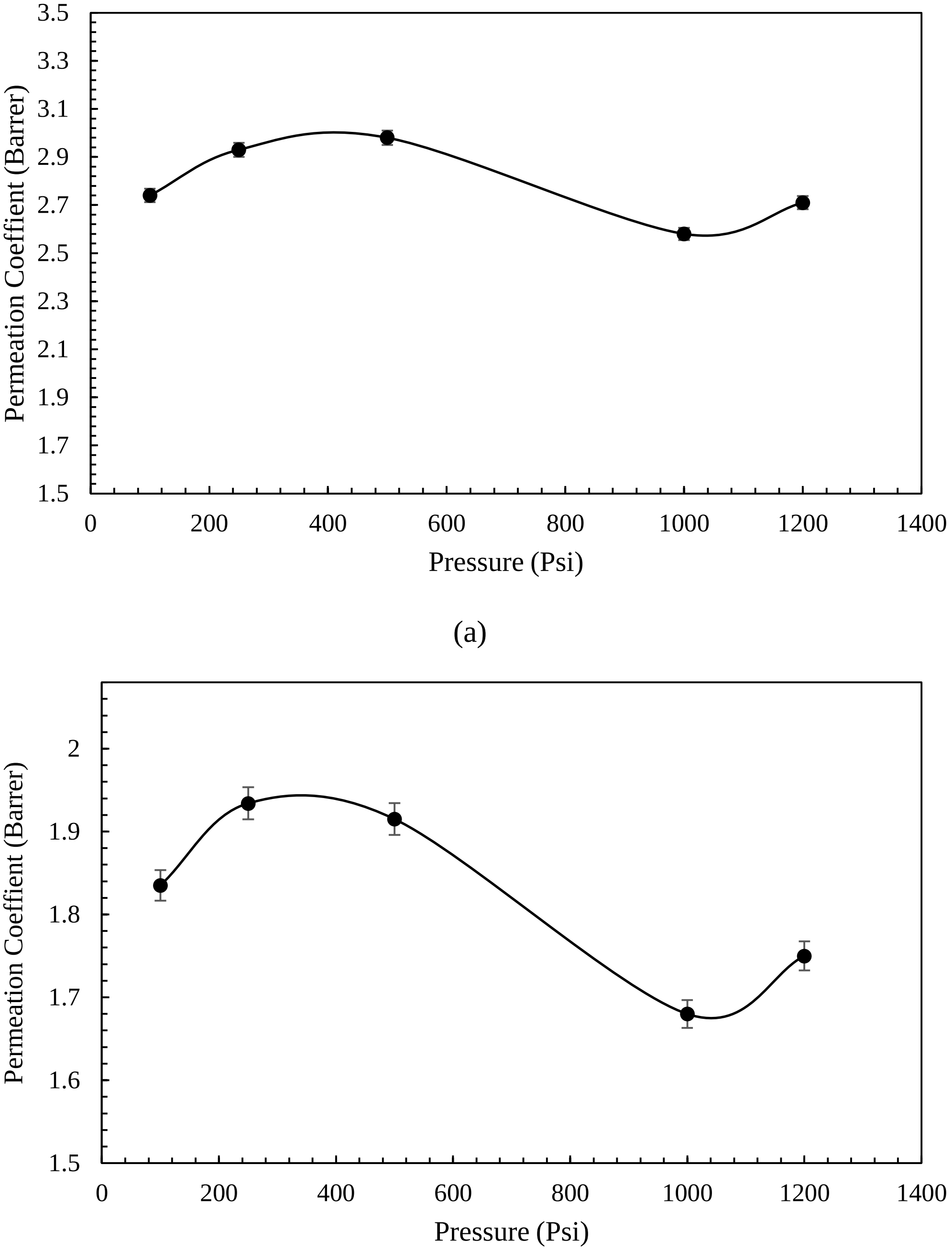


Figure 11: Effect of pressure on gas permeation coefficient for Viton (H)

The change in gas permeation due to pressure increase is not significant. Gas permeation coefficient ranged from 1.6 Barrer to 2 Barrer by increasing gas pressure from 100 Psi to 1200 Psi. These results are compatible with what has been observed in previous research about pressure effect on gas permeation.

Newitt et al. [30] performed experiments at up to 300 atm (4400 Psi). They studied solubility and diffusion individually and observed an increase in solubility coefficient by increasing pressure. While diffusion coefficient was not affected by pressure. Campion and Morgan [34] ran experiments up to 5000 Psi. They observed a minor reduction in gas permeation at higher pressures. Klopffer et al. [33] experiments were carried out at pressures up to 20 Bar (300 Psi). In their experiments, no effect on gas permeation was observed by increasing pressure.



(a)

(b)

Figure 12: Effect of pressure on gas permeation coefficient for (a) Viton (R) (b) Viton (H)

As it is illustrated in Figure 12, in both polymers a general behavior was observed. At the beginning, increasing pressure led to an increase in gas permeation, and permeation went to a maximum. Although by a further increase in pressure, a minimum was observed at 1000 Psi.

In low pressure condition experimental results showed that gas solubility was a function of temperature and temperature has an insignificant effect on it [7]. However, Newitt et al. results showed that increasing pressure leads to an increase in solubility coefficient [30].

Gas permeation reduction at higher pressure may be due to a pressure-induced compaction of polymer, causing its molecular chains to pack closely together. Therefore, the free volume available within the polymer decreases which is in direct correlation with gas permeation [46, 34]. By further increasing of gas pressure, the gas permeation increased again. Increasing gas permeation after observing a minimum can be due to solubility increase overcoming the reduction in the free volume of the polymer.

4.4 Summary of the Chapter

The effect of pressure and pressure on gas permeation has been investigated in various studies. The results obtained in the current research showed that temperature has a significant effect on gas permeation. On the other hand, the pressure effect was insignificant. Increasing the temperature led to significant rise in gas permeation which may be due to increase in the fractional free volume of the polymer at higher temperatures. While increasing pressure caused an insignificant change in the permeation. In both tested polymers, the pressure increase led to observing a maximum and then a minimum in permeation by a further increase in the pressure. The two processes behind the permeation, gas solution and gas diffusion process, are affecting in different ways by pressure. Increasing pressure leads to an increase in gas solution and reduction in gas diffusion. Therefore, different permeation behavior may be observed depending on the pressure acting on the polymer.

CHAPTER 5: PREDICTING GAS PERMEATION

Various studies have investigated gas permeation mechanism and measured gas permeation coefficient for different gasses through a wide range of polymers. Those experiments helped learning about the principles governing the gas permeation process and the parameters affecting gas permeation. By using the experimental results, an effective tool can be developed to predict gas permeation for such conditions where no experimental data exists. Several studies have been conducted to predict gas permeation based on the characteristics of the polymer such as the fractional free volume of the polymer, or by using parameters affecting gas permeation [1, 2, 6, 41, 45, 47]

As it was observed in chapter 4, the temperature has a significant effect on gas permeation. Therefore, correlating temperature and permeation coefficient can be helpful to develop a predictive tool for gas permeation.

In this chapter, a permeation model will be described as the predictive tool. And the results obtained from performed experiments will be used to verify the accuracy of the predictions.

5.1 The Arrhenius Equation

Temperature has always been one of the significant effective parameters in chemical reactions. Arrhenius has used Van't Hoff's research about the effect of temperature on the rate of chemical reactions to formulate an equation. He has mathematically described the relationship between a chemical reaction rate and temperature as follows [48]:

$$K(T) = K(T_{ref})Exp[\frac{E_a}{R}(\frac{1}{T_{ref}} - \frac{1}{T})] \tag{Eq. 17}$$

Or

$$Ln\left[\frac{K(T)}{K(T_{ref})}\right] = \frac{E_a}{R}(\frac{1}{T_{ref}} - \frac{1}{T}) \tag{Eq. 18}$$

Where:

$K(T)$: Reaction rate at temperature T
$K(T_{ref})$: Reaction rate at a reference temperature
E_a: Activation energy of the reaction (J, kJ, cal, or kcal per mole)
R: Universal gas constant (J/K.mole, kJ/K.mole,… in corresponding units)
T: Temperature (Kelvin)
T_{ref}: Reference temperature (Kelvin)

By plotting Ln [k(T)] vs $\frac{1}{T}$; a straight line should be obtained. The slope of this straight line has been used to estimate the activation energy of the chemical reaction as follows:

$$E_a = R\frac{d(LnK(T))}{d(\frac{1}{T})} \tag{Eq. 19}$$

Arrhenius relationship has been used and verified in various fields. It is widely used to predict the rate of change of different reactions from food degradation to gas diffusion and permeation [5, 7, 49-56].

5.2 Permeation in Arrhenius Relationship Format

Barrer [14] has shown that both solubility and diffusion coefficient obey the Arrhenius relationship. By considering infinite temperature as the reference temperature and using Eq. 17, following relationships obtained to be used:

$$S = S_0 \exp(-\frac{\Delta H_s}{RT}) \qquad \text{Eq. 20}$$

$$D = D_0 \exp(-\frac{E_D}{RT}) \qquad \text{Eq. 21}$$

Where $S_0$and D_0 are solubility and diffusion coefficients at a reference temperature. Barrer has considered the reference temperature as infinity. ΔHs is the heat of solution and E_D is the activation energy for diffusion, R is the gas constant and T is the absolute temperature [34]. Referring to Eq. 6 permeation coefficient can be described by the following equation:

$$P = D \times S = D_0 S_0 \exp(-\frac{\Delta H_s + E_D}{RT}) \qquad \text{Eq. 22}$$

$$P = P_0 \exp(-\frac{E_p}{RT}) \qquad \text{Eq. 23}$$

Where P_0 is the permeation coefficient at the reference temperature, with a constant value, and E_p is the activation energy of permeation:

$$E_p = \Delta H_s + E_D \qquad \text{Eq. 24}$$

The important assumption made by Barrer is that the activation energies are constants and do not depend on the temperature. This assumption has been verified to be true for a temperature range of 25˚C to 50˚C, but various studies have also used the Arrhenius relationship for calculating permeation at higher temperatures [52, 54, 56, 57].

5.3 Fitting Arrhenius Equation to the Experimental Results

In the current study, the obtained experimental permeation coefficients were plotted versus $\frac{1}{T}$ in order to find the permeation Arrhenius equation, Figure 13 and Figure 14. By fitting an exponential equation to the data, the Arrhenius equation was achieved.

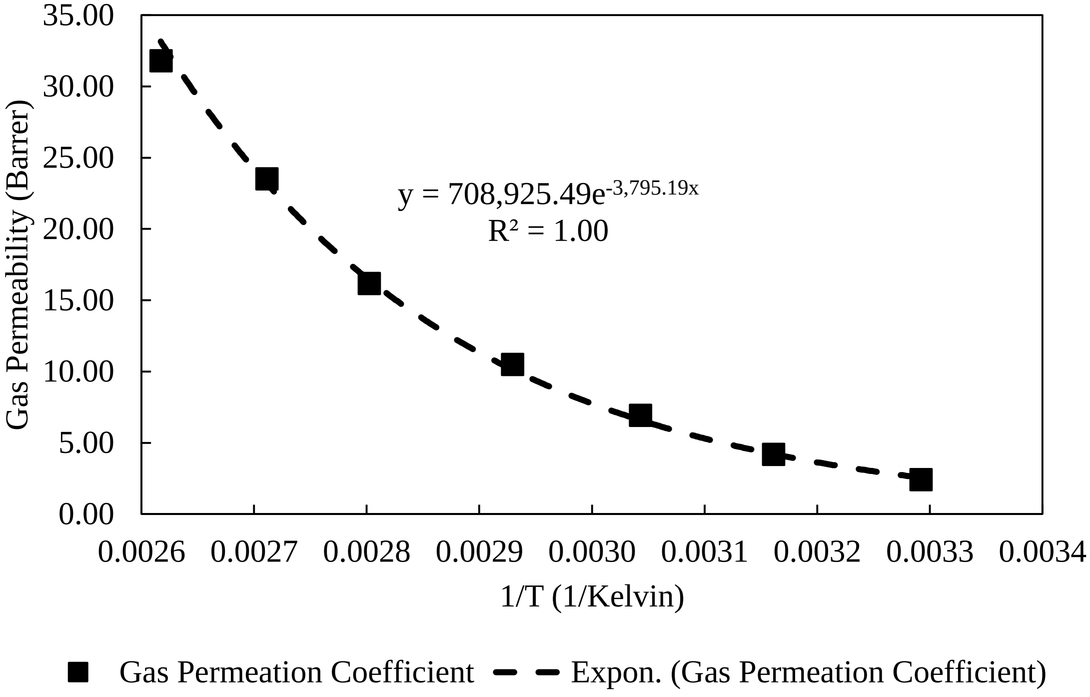


Figure 13: Gas Permeation Coefficients in Arrhenius Format at 1200 Psi

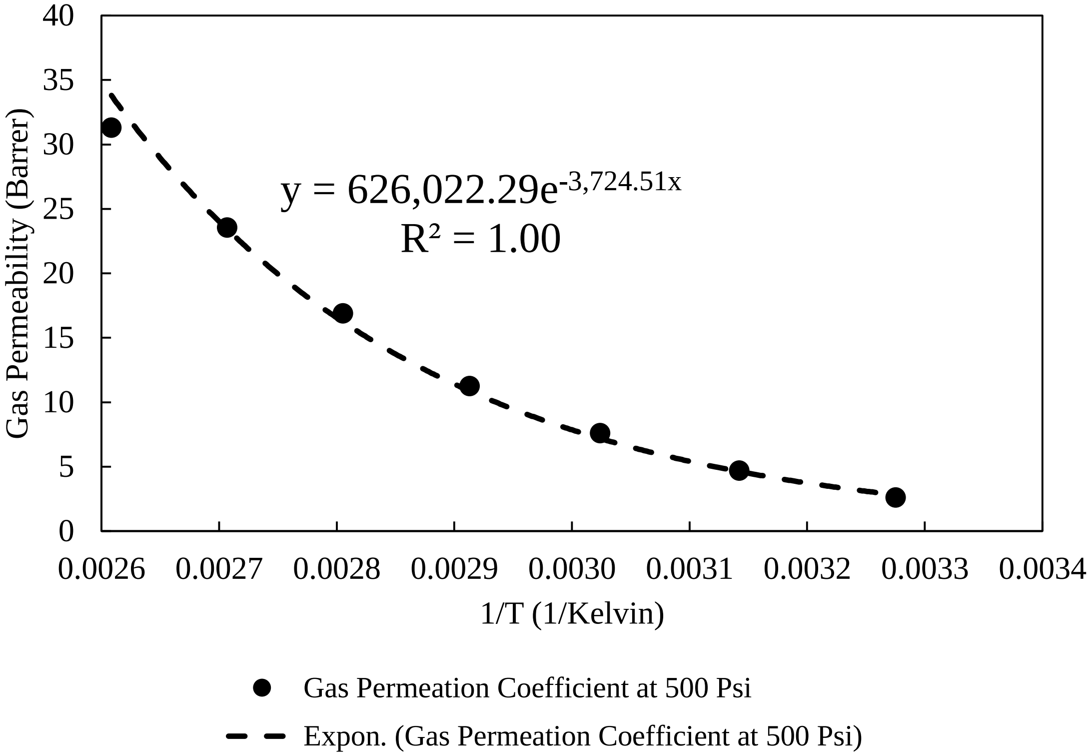


Figure 14: Gas Permeation Coefficient in Arrhenius format at 500 Psi

Figure 13 and Figure 14 show that the change in the rate of permeation coefficient over the temperature range of 30˚C to 105˚C obeys an Arrhenius equation at both high pressure and low pressure conditions. A close fit can be observed all over the temperature range, although for low values of 1/T (high temperature condition) the maximum deviation was noticed. As mentioned earlier Barrer assumed activation energies are independence from the temperature which may not be true for high temperatures. Therefore the reason behind increasing deviations at a higher temperature could be the change in related activation energy [29].

Using obtained Arrhenius equations, permeation coefficient can be calculated. Figure 15 and Figure 16 illustrate the normal distribution of predicted permeation by obtained

Arrhenius equations versus the experimental results. It can be observed that the normal distribution of these coefficients is close to a 45° line and the calculated coefficients are in good agreement with experimental results.

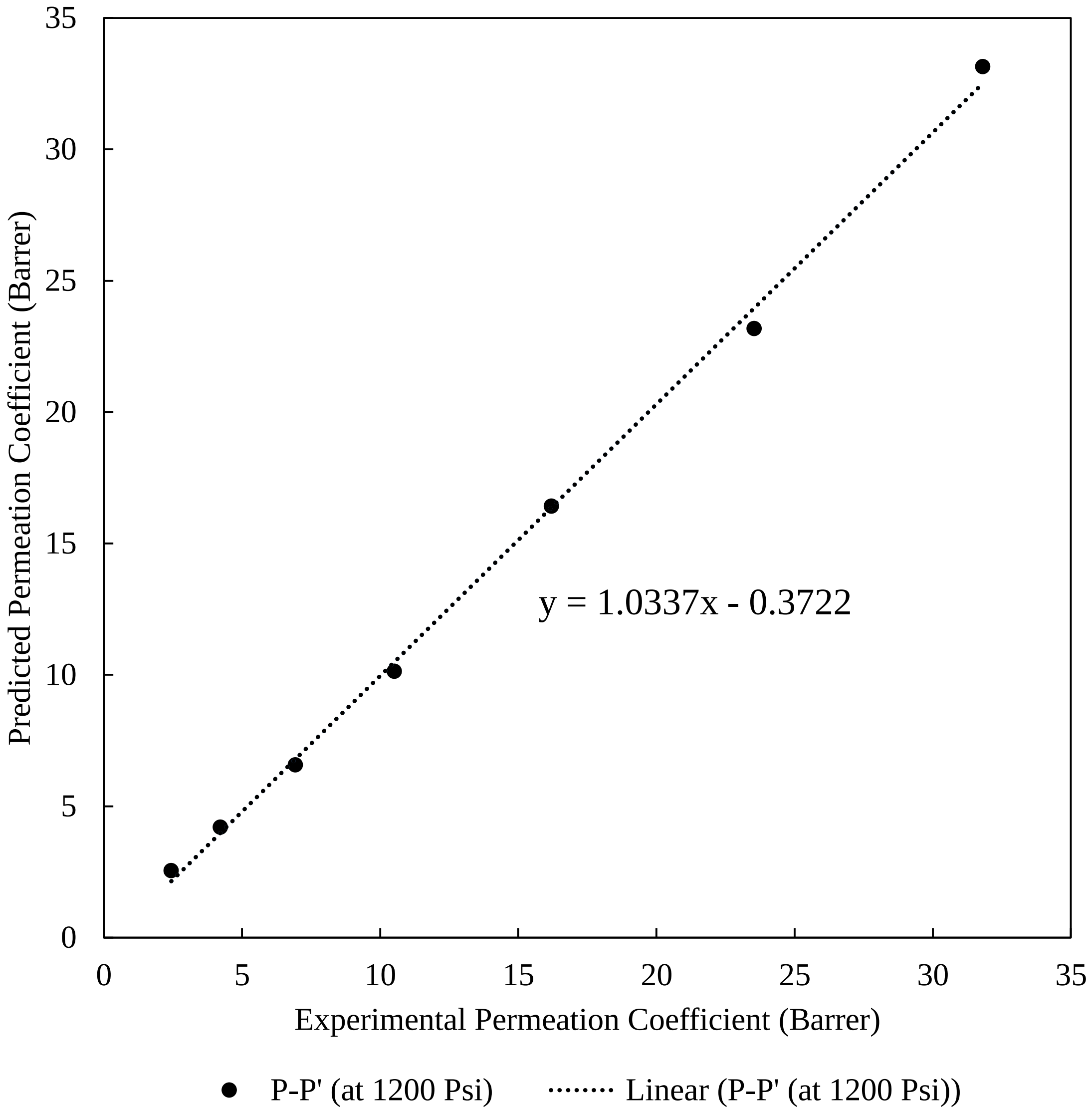


Figure 15: Comparison of the predicted permeation coefficients to obtained results from the permeation experiments at 1200 Psi

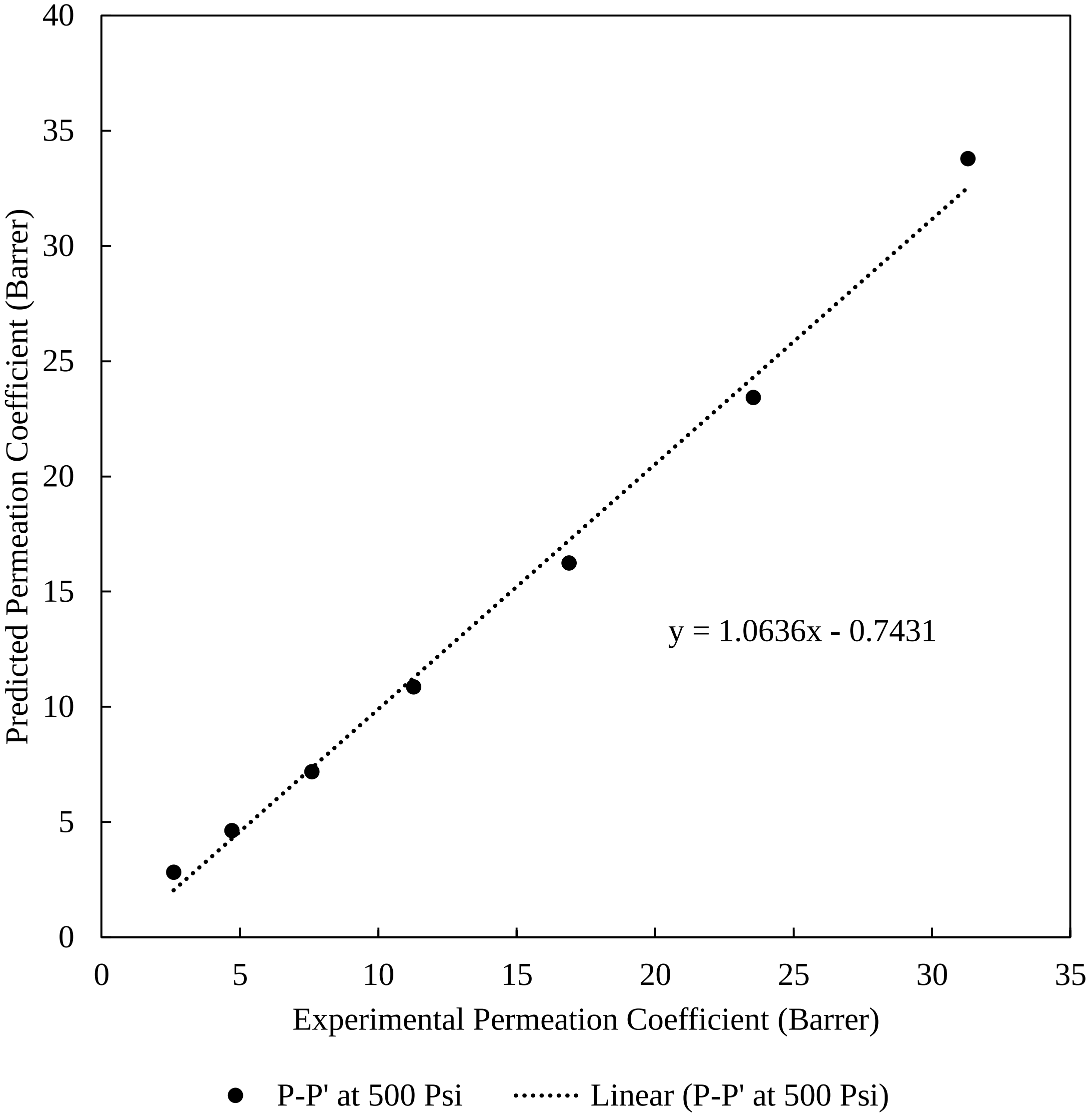


Figure 16: Comparison of the predicted permeation coefficients to obtained results from the permeation experiments at 500 Psi

By using the obtained Arrhenius equations for permeation, the permeation activation energy of Viton can be estimated. The obtained activation energies are displayed in Table 5.

Table 5: Activation energies obtained for Viton

	$P(T) = P_0 \exp(-\frac{E_p}{RT})$ $\mathrm{R} = 1.985877\mathrm{E}-3\frac{Kcal}{K.mole}$	
P = 1200 Psi	$P(T) = 708925.49 \exp(-\frac{3795.19}{T})$	$E_P = 7.537 \frac{Kcal}{mole}$
P = 500 Psi	$P(T) = 626022.29 \exp(-\frac{3724.51}{T})$	$E_P = 7.396 \frac{Kcal}{mole}$

It is observed that the change in the calculated activation energies at different pressures is insignificant. These results are in a good agreement with what was observed in the experiments about the insignificant effect of the pressure. In order to test if the equation for one pressure can be generalized to a wider range of pressures, the permeation coefficients at each high and low pressure conditions were calculated by the Arrhenius equations related to the other pressure condition. The results are displayed in Figure 17 and Figure 18. As it is illustrated in the plots, the results are very close and both obtained permeation relationships can be used to give an estimate of gas permeation at different temperatures and pressures for the Viton material used in the experiments. As experimental permeation coefficient increases the difference between predicted permeation and experimental coefficient grows. As mentioned before, the activation energy depends on the temperature which can be the reason for the observed deviations.

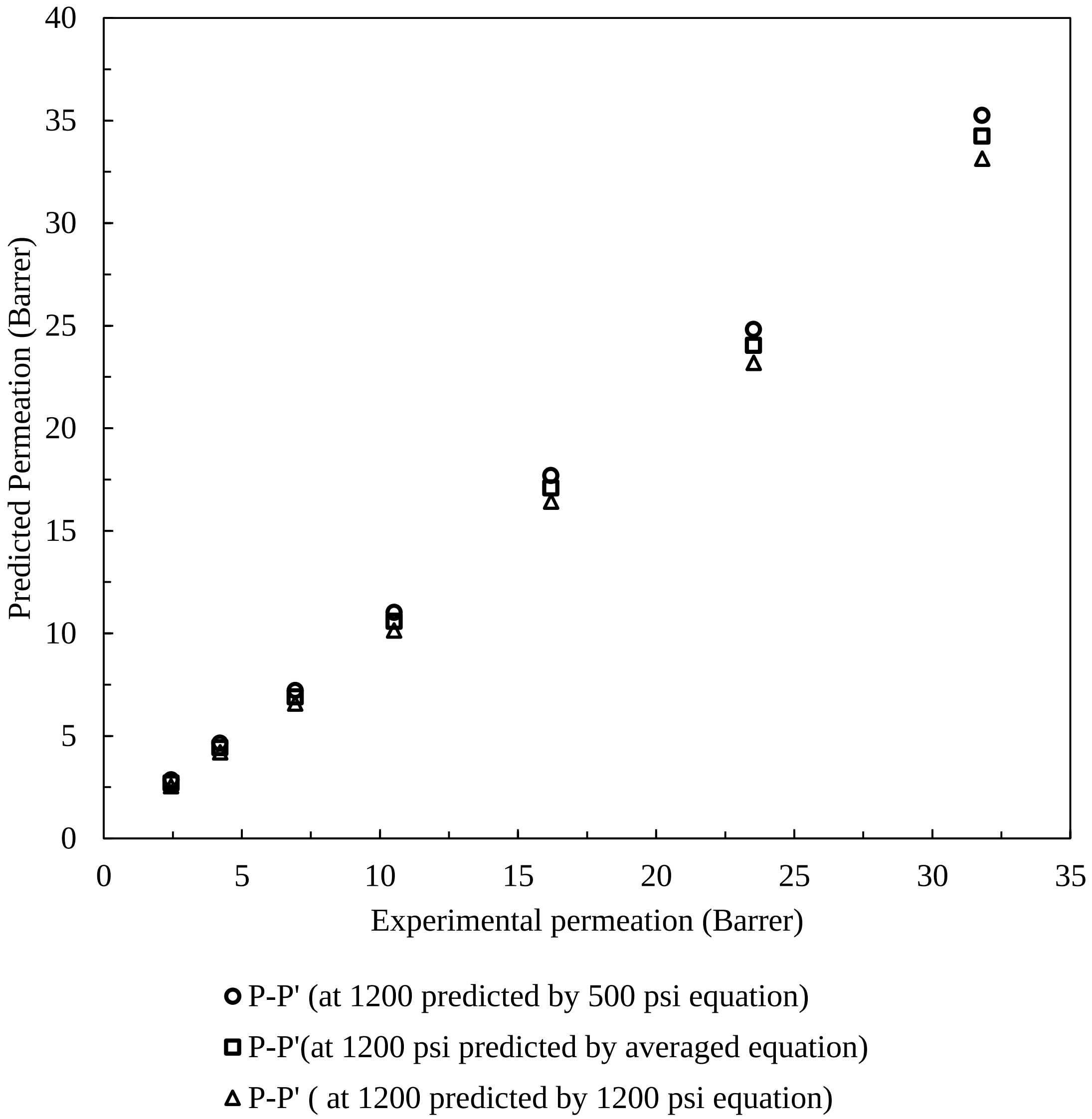


Figure 17: Comparison of predicted gas permeation coefficients using equation of different pressure condition

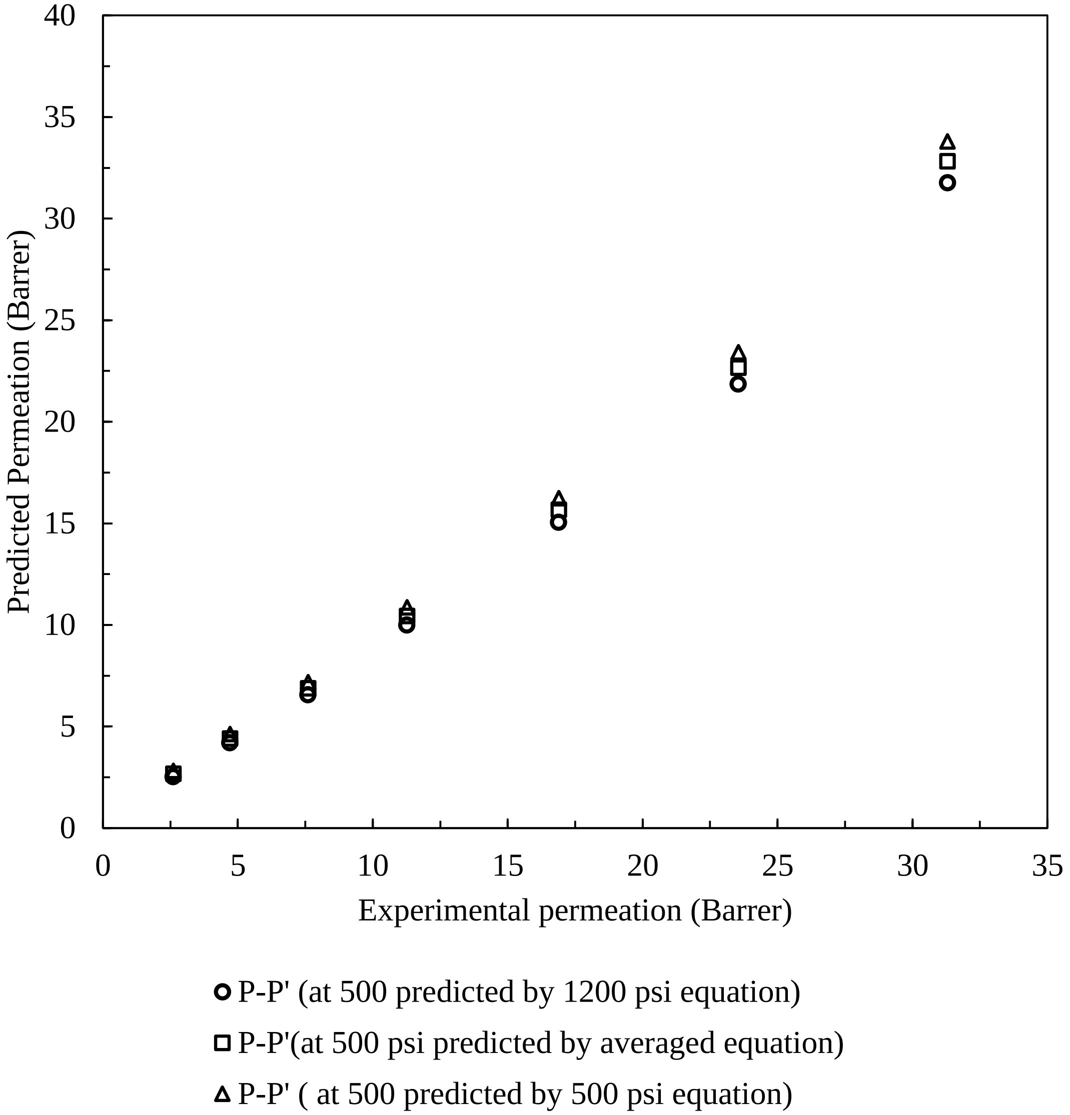


Figure 18: Comparison of predicted gas permeation coefficients using equation of different pressure condition (500 Psi)

5.4 Summary of Chapter

By using Arrhenius relationship for gas permeation rate, two predictive models were obtained for two different pressures over a temperature range of 30˚C to 105˚C. It was observed that pressure does not have a significant effect on the prediction model. The predicted permeation using both models were close and applicable to both high and low pressure conditions. The obtained equations can be used to have an estimation of gas permeation for temperatures where no experimental data exists.

CHAPTER 6: ENHANCING BARRIER PROPERTIES

Polymers are replacing other material such as metals, paper, and ceramics in various industries due to the ease of production and lower cost. However, compared to some of their competitive materials such as metal and glass, the rate of gas transfer in polymers can be improved. Therefore, the interest in enhancing barrier properties of polymers has been increased in recent decades. Two most common methods used to improve barrier properties of polymers are applying a surface coat and embedding nanoparticles in the manufacturing process of the polymers.

One of the research objectives of this study was to find a method to decrease gas permeation in the polymeric membranes. The main goal was to find method needs to be simple enough to be applied in field operation, not in a laboratory. Therefore, coating the polymer was selected as the solution for barrier improvement. In a preliminary study, several materials were studied to select the coating material. Finally, two components elastomeric silicon and a high temperature resistant paint were selected to be applied as the coating material. The study was expanded to include the effect of adding Nanoparticles to the coating. In this chapter, the experimental results for applying the coatings will be discussed.

Furthermore, a new method of decreasing gas permeation through a polymer will be explained. In this method, a thick layer of hydraulic oil was added to the permeation barrier system in order to decrease the gas transfer to the low pressure side of the permeation cell. The results and efficiency of all three methods will be explained in the following sections.

6.1 Coating Polymers

The application of the coating on polymers has been investigated by various researchers. Thin layers of different coatings have been applied on the surface of polymers to increase the barrier properties against gases. History of implementing coatings on polymers can be traced back to late 1950's when Prins et al. [58] studied the effect of adding a metal coating to polymers in 1958. They gave a theoretical solution for gas permeation through defects in a metal coating and tried to predict gas flux in the coated polymers. The effect of adding metal and metal oxide coating has been investigated in a number of studies [59-62]. One of the weaknesses of the metallic coatings is the existing of pinholes and fractures in the coating [63]. Elastomeric coatings are flexible and can be a proper substitute for solving the fracture problem [64-68]. The most common flexible coatings used are silicone based coatings. Lay et al. [67] examined thin film of silicon oxide and silicon nitride as flexible coatings for flexible electrical equipment and their results showed that these two materials can be good candidates for barrier improvement to be used on flexible equipment. Lin et al. [69] showed the improvement in barrier properties of polyethylene polymers against oxygen and water vapor permeation after applying transparent silicone oxide coating. Roberts et al. [69] investigated the permeation in Nano defects existing in the silicon oxide coatings. Therefore, they suggested that silicone coating should be considered as Nano-porous. Roberts et al. [69] also proposed a model for gas permeation in the silicone coatings by assuming that the coating is acting as a Nano-porous material.

The probability of having defects in a single layer of coating is high. Thus, many studies have been conducted to investigate the effect of multilayer coatings or adding materials to the coating in order to improve gas permeation barrier properties. Nanoparticles and Micro sized impermeable particles are widely used to enhance coating properties. By adding clay particles to the polymers, significant improvements have been observed in a variety of material properties such as mechanical properties, thermal properties and barrier properties [70]. The main goal of adding particles to the coating is to form a longer pathway for the gas molecules to transfer and make permeation through the coating harder [52, 71]. It has been reported that by adding clay particles to the polymers gas permeation can be reduced by 50 to 500 times [72]. Yano et al. [73] were able to reduce the permeation of different gasses to less than half by implementing clay particles in the polymer. While Lape et al. [74] observed 10-100 times smaller permeation in polymeric films after implementing impermeable flakes. Ogasawara et al. [75] reported a reduction in gas permeation by adding Nanoparticles. Although they observed a decrease in the gas diffusion while the gas solubility increased. Numerous studies tried to model the permeation through polymers with added particles by using the volume fraction and orientation of the particles [3, 76, 77].

Despite the successful results of adding particles in order to reduce gas permeation in polymers. This method needs to be performed with high accuracy and needs to be implemented in a controlled setting by operators with professional skills. There are coatings, such as paint coatings, available that enhance material properties and at the same time are simple to be applied such as paint coatings.

Paint coatings are widely used as oxygen and water vapor barriers in metal protection, wood rotting, and food packaging [16]. Paint structure is made of a binder, pigment solvents and additive materials. The main element of paint coatings is the binder which specifies most of the paint characteristics. The pigments are responsible for the color, opacity and gloss, and protective or barrier properties of the paint [78]. Thomas [16] has investigated the permeability in paint coatings and reported that some paints are better barriers compared to the polymers such as PET, PVC, and PVF.

Different types of pigmentation in the paint can result in improvement or diminishing barrier properties of the coating. Parameters such as the impermeability of the pigments, aspect ratio of pigments, and the quality of the adhesion between pigment and the binder impact the efficiency of pigmentation significantly [79]. The change in the volume of the pigments in a paint coating can lead to alteration of its characteristics. The pigment volume concentration (PVC) is the ratio of the pigments volume to the total volume of all elements forming the paint. PVC is a fundamental physical property of the paint and has been investigated in various studies [16, 79-82]. These studies have shown that increasing the volume of the pigments in the paint film can result in improvement of the permeation properties. Although after a certain point, called the critical pigment volume concentration or CPVC, the improvement stops and permeation increases [16, 80]. Figure 19 illustrates the effect of PVC on the permeability of paint coating.

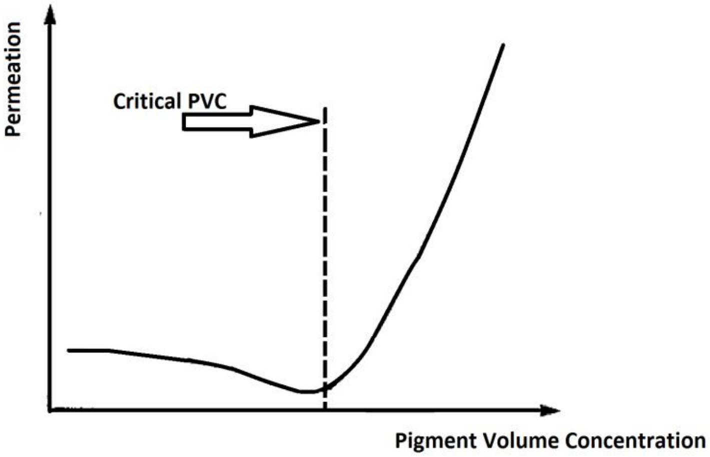


Figure 19: Pigment Volume Concentration effect on permeation in paint films [16]

6.2 Experimental Results

6.2.1 Elastomeric Silicone Coating

6.2.1.1 Material and Sample Preparation

The coating was applied to two different type of fluoropolymer elastomers, Viton (L) which is used in the oil and gas industry as protection against gas and moisture permeation and Viton rubber sheets. Viton rubber sheets with the hardness of 75 Durometer is available commercially and was purchased through a US manufacturing company, Select. The elastomeric material used for coating was Sylgard 182, a liquid silicone elastomer material. Sylgard was obtained from Dow Corning Corporation. It is usually used for protecting flexible electrical equipment.

The coating is supplied in two parts, the base, and the curing agent. The compartments should be mixed in a ratio of 10 part base to 1 part curing agent. After mixing thoroughly at 400 rpm for 10 minutes using an electronic mixer, the mixture was placed in a vacuum oven for 30 minutes to remove any air bubble trapped in the mixture during the mixing process.

The samples placed in an oven at a temperature slightly higher than room temperature (45˚C) for at least 12 hours in order to remove any moisture absorbed in them. Then the membranes were cleaned using a Dow Corning primer. After cleaning the samples, the coating was applied using fine paint brushes. Samples were placed to rest for another half an hour to remove any air bubbles. As the final step, the samples were placed in the oven to start the curing process. Once curing completed, Sylgard formed a transparent elastic coating. The samples were stored in moisture proof bags until testing.

In a preliminary study, several Nano and Micro sized particles were added to the Sylgard and their effect on permeability was examined. Adding some particles to silicone base led to an increase in permeation coefficient of the coated samples. Although, adding some other particles led to failure in the curing process of the Sylgard. The list of the tested particles and the result of adding them to Sylgard is reported in Table 6.

.

Table 6: List of the Nanoparticles used in the preliminary study

	Moisture	Typical Dry Particle Size	Packed Bulk Density	Density	X Ray Results	Adding to Sylgard
	%	µm (d50)	g/l	g/cm3	nm	
Cloisite CA++	4-9	<10	625	2.8	1.55	Successful
Cloisite NA+	4-9	<25	568	2.86	1.17	Successful
Cloisite 10A	<3	<10	265	1.9	1.9	Failed
Cloisite 11B	<3	<40	265	2	1.84	Failed
Cloisite 15	<3	<10	165	1.66	3.63	Failed
Cloisite 20	<3	<10	175	1.77	3.16	Failed

CLOISITE CA++ was successful in gas permeation reduction. Therefore, it was selected to be used in the experiments. CLOISITE Ca++ was purchased from Dow Corning Corporation. Cloisite CA++ is “an additive for plastics and rubber to improve various physical properties, such as reinforcement, CLTE, synergistic flame retardant and barrier” [83]. In the preliminary study, different percentages of particle weight (from 1 to 5 percentage) were tested in order to find the optimum amount of added particles. Finally, four percent of the total weight was selected as the optimum value of particle weight to be mix with the silicon coating and form an elastomeric coating with randomly oriented flakes.

The particles were weighed using an analytical balance with the readability of 0.0001 grams. The weighted particles were added to the Silicone base and mixed at 400 rpm for 20 minutes. Then the curing agent was added and the mixing process continued for another 10 minutes. The rest of the sample preparing procedure was similar to the procedure for Sylgard with no added particles.

6.2.1.2 Experimental Results

Permeation experiments for the commercial Viton were performed at three temperature and two pressure condition. Due to a shortage of samples for Viton (L), the experiments were carried out only at the high-pressure condition and Sylgard coating. Commercially purchased Viton was used for the comprehensive study of the coating effect. The design of the experiments is displayed in Table 7 and

Table 8. The permeation coefficients obtained from experiments are plotted in Figure 20, Figure 21, and Figure 22.

Table 7: Design of the Experiments (DOE) for coating experiments on commercial Viton

Coated Polymer						Non-Coated Polymer					
Pressure						Pressure					
500 Psi			1200 Psi			500 Psi			1200 Psi		
Temperature						Temperature					
30˚C	75˚C	100˚C	30˚C	75˚C	100˚C	30˚C	75˚C	100˚C	30˚C	75˚C	100˚C

Table 8: Design of Experiments (DOE) for coating experiments on Viton (L)

Coated Polymer		Non-Coated Polymer	
Temperature		Temperature	
30˚C	100˚C	30˚C	100˚C

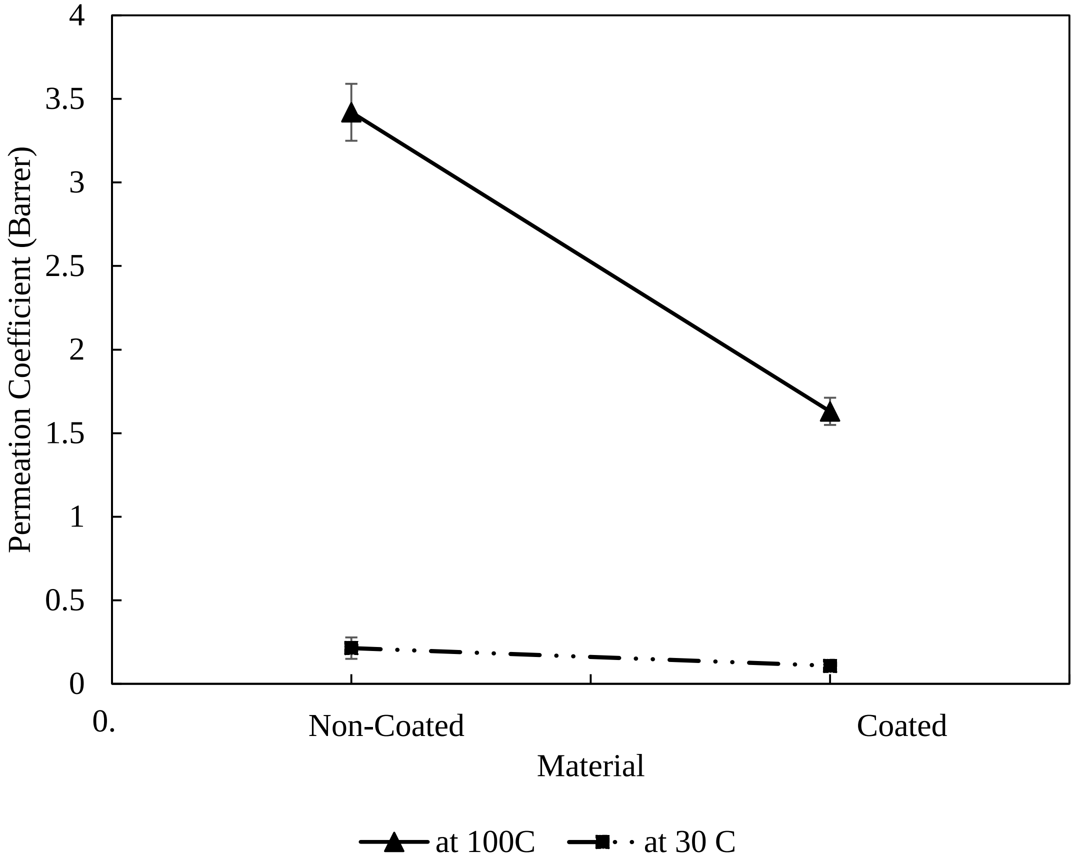


Figure 20: Gas Permeation in non-coated and coated Viton (L) at two temperatures

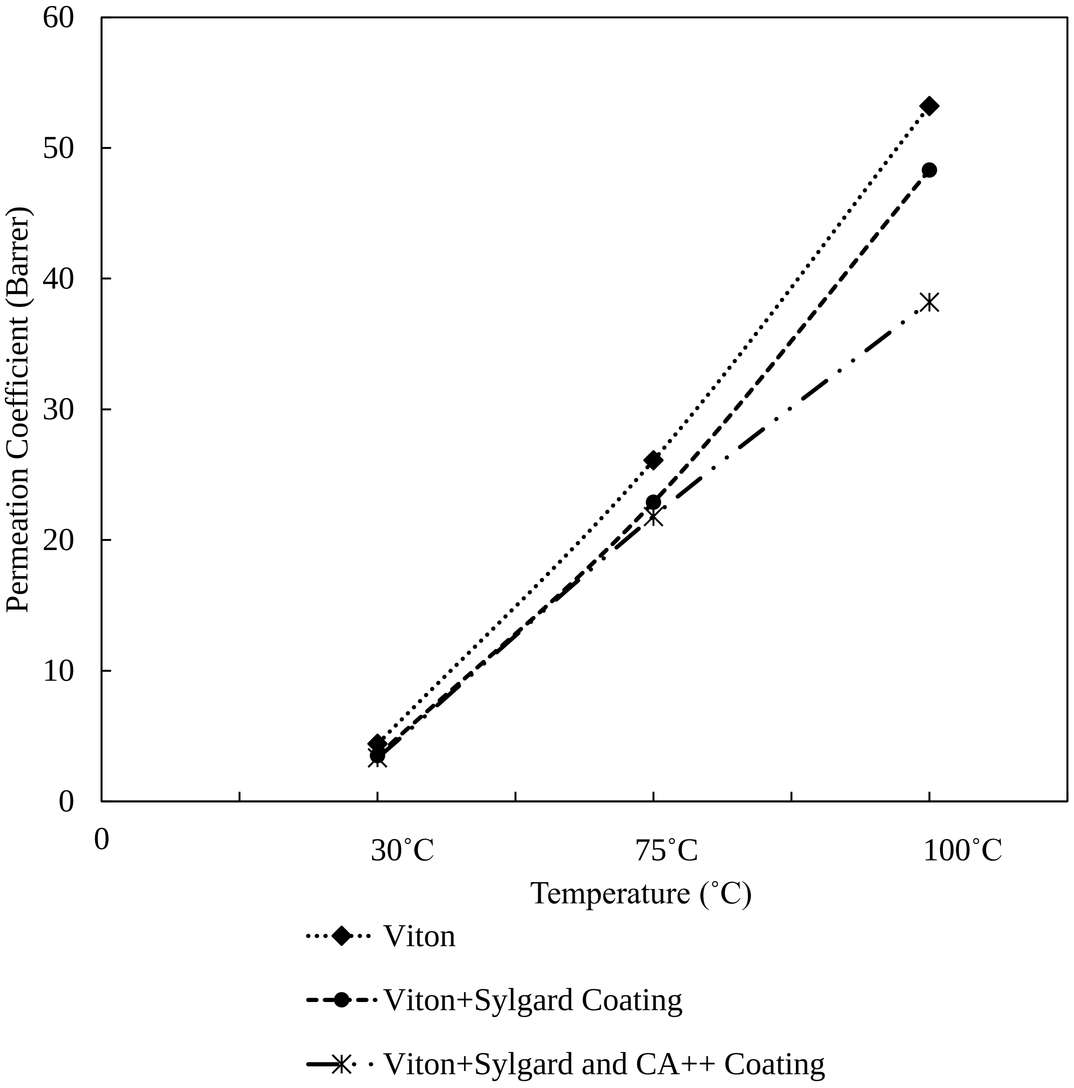


Figure 21: Gas permeation in coated commercial Viton at 500 Psi

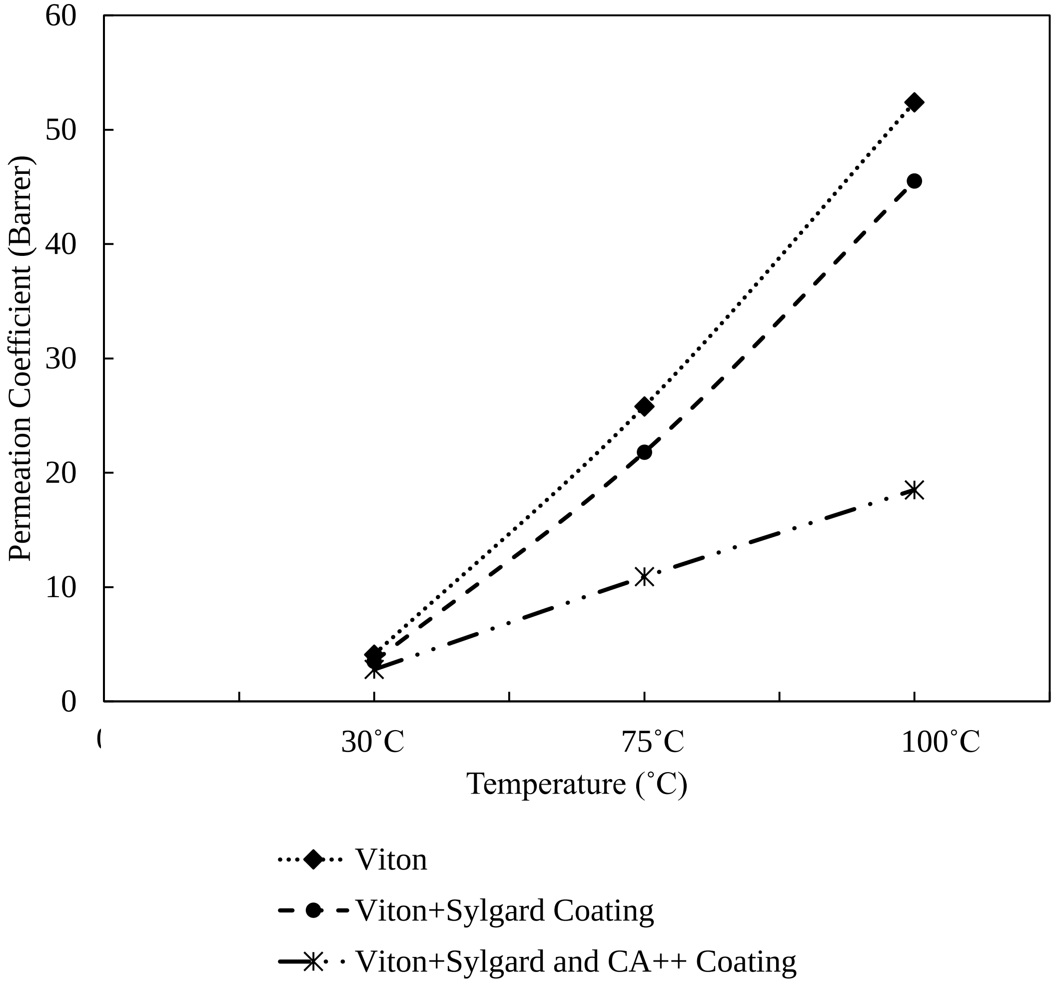


Figure 22: Gas permeation in coated commercial Viton at 1200 Psi

Figure 20 displays the results for coated Viton (L). The obtained results at two temperatures (30˚C and 100˚C) are included in the plot. The permeation was reduced to less than half in both temperature conditions.

Figure 21 shows the effect of different coatings on Viton rubber sheet at 500 Psi. As it is displayed in the plot, the Sylgard coating reduced the permeation in the sample. The reduction in gas permeation was in a range from 10% at high-temperature to 20% at the low-temperature condition. The reduction in the Viton rubber sheet was significantly than the reduction by 50% in Viton (L). Also, the plot includes the permeation results for Sylgard plus CA++ coating. It can be seen that the differences in the permeability of two coating are insignificant at 30˚C and 75˚C. The reduction in permeability coefficient was around 5% at 30˚C and 75˚C. However, by increasing the temperature, the Sylgard with added clay particles displayed better barrier properties compared to Sylgard coating. At 100˚C, adding particles to Sylgard led to an improvement of 28% at 500 Psi and 46% at 1200 Psi. It might be due to higher activation energy in the coating with the added particles. As mentioned in chapter 4, in higher temperature conditions the fractional free volume of the material increases. By adding particles to the coating, the holes in the coating was filled by particles and the effect of temperature on free volume decreased. Therefore, at higher temperatures the free volume of Sylgard with added particles increased but less than the free volume of Sylgard coating. The less increase in free volume leads to exhibiting of better barrier properties.

Figure 22 shows similar trends to Figure 21. However, the effect of adding clay particles is more significant. Sylgard with added particles displays well-improved performance at 1200 psi compared to 500 Psi. The free volume in the Sylgard coating may reduce after adding particles. It can be the reason behind more reduction of gas permeation in the Sylgard with added particles compared to Sylgard coating. As it was concluded in section 4.3, increasing pressure may lead to a reduction in the free volume of the polymers. Therefore, better improvement at higher pressures may be due to more reduction in the free volume of the Sylgard plus CA++ coating.

6.2.2 Paint Coating

6.2.2.1 Material and Sample Preparation

Paint coatings are simple to apply compared to other methods of coating. Lower cost and ease of application of paint coating turn them to excellent choice to be used in the field. A high-temperature resistant paint was selected to be applied to the polymeric samples. The paint was purchased from Rust-Oleum Corporation. It composed of a modified silicone binder and black Manganese Ferrite pigments. The selected paint can resist temperatures up to 650˚C.

The Viton(R) rubber sheet with a hardness of 70 Durometer hardness was used for examining the paint coating. Viton was purchased from E. James Company.

Before applying the paint, the sample surfaces were cleaned using an alcoholic base cleaner liquid. Then, the samples were placed in a 45˚C oven for 12 hours to remove the moisture absorbed in them. After de-moisturizing the samples, the paint coat was applied on the samples. Each sample was coated with three layers of paint. The drying time of each layer was 48 hours [84].

6.2.2.2 Experimental Results

The coated samples were tested at three different temperatures, and two levels of pressure. The design of the experiments for paint coated samples is shown in Table 9. The experimental results are displayed in Figure 23 and Figure 24.

Table 9: Design of Experiment for Paint Coating Samples

Pressure					
500 Psi			1200 Psi		
Temperature			Temperature		
30˚C	75˚C	100˚C	30˚C	75˚C	100˚C

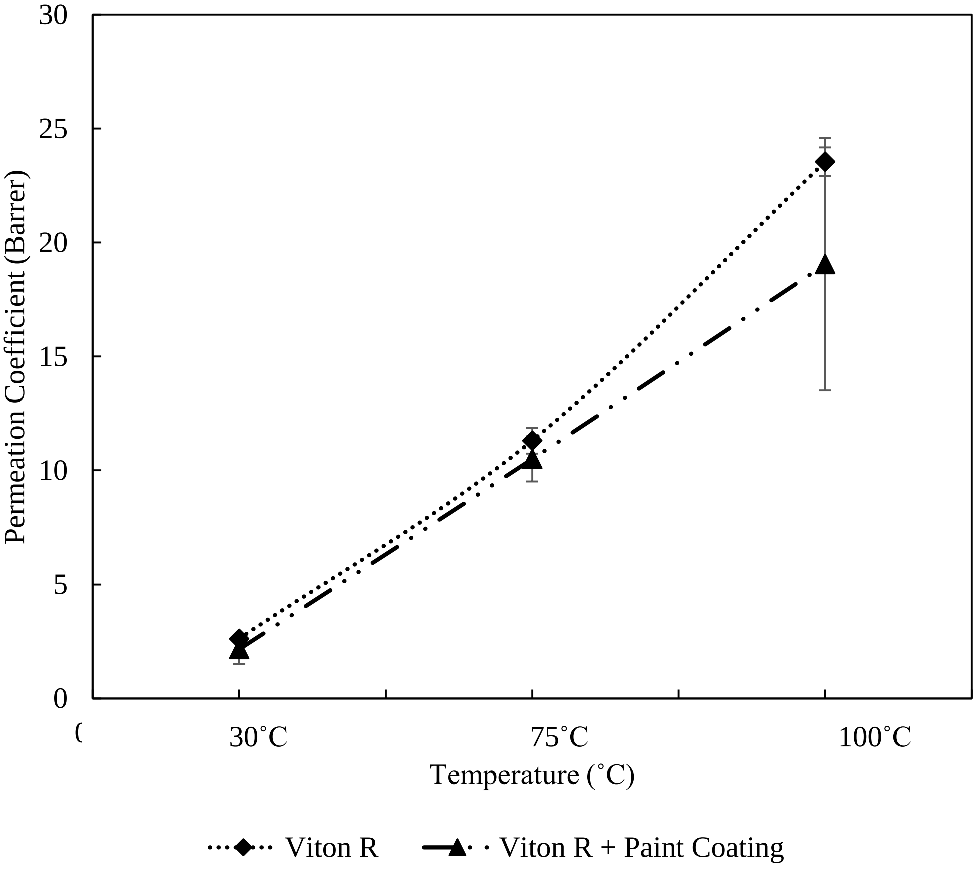


Figure 23: Gas permeation in paint coated Viton B at 500 Psi

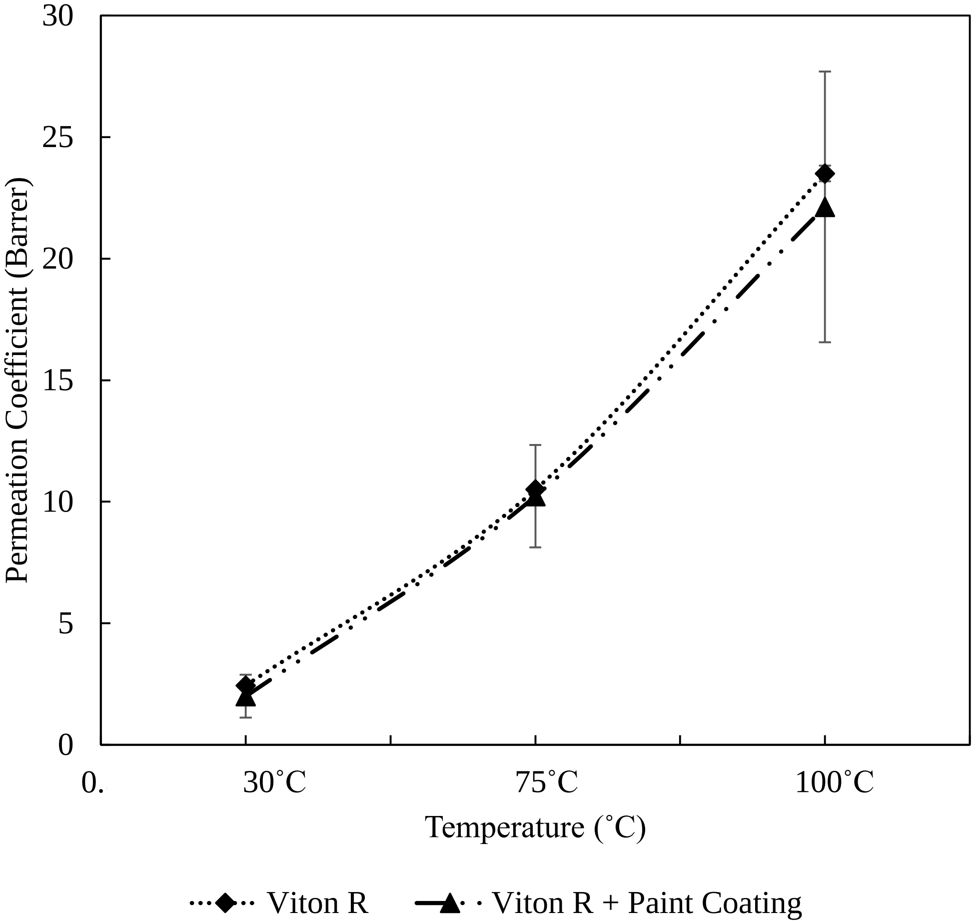


Figure 24: Gas permeation in paint coated Viton B at 1200 Psi

The results showed insignificant improvement by applying the paint coating. The coating performance was more efficient at a higher temperature. The improvement ranged from 3% to 19%. The maximum improvement of 19% happened at 500 psi and 100˚C. The deviations of the results obtained from painted samples were large. The large deviations in the obtained results may be a result of the quality of the applied paint coating. Painting the samples has been done manually and it had randomly distributed flaws. By looking at each experiment individually, there were some cases of reduction in permeation by 35%.

An interesting observation made in the paint coated experiments was the difference between the starting times of the permeation process. Coating samples by paint delayed the start of permeation process. As mentioned in Chapter 2, permeation is a three steps procedure, Solving-Diffusing-Dissolving. After gas molecules start to dissolve from the membrane, the increase in gas pressure can be observed on the downstream side of the membrane.

Figure 25 and Figure 26 show the change in the pressure in the downstream chamber of the permeation cell in a non-coated sample and a coated sample. It can be observed in the plots that pressure in the downstream (Low Pressure) chamber stays constant for a while and then it starts to increase with a uniform slope in both coated and non-coated sample. But as it can be seen the starting point of coated samples happened later than the non-coated sample. The starting time has increased by nearly three times, from 400 seconds to 1300 seconds. The delay in the start of permeation process is a significant improvement that can be effectively implemented for short time application.

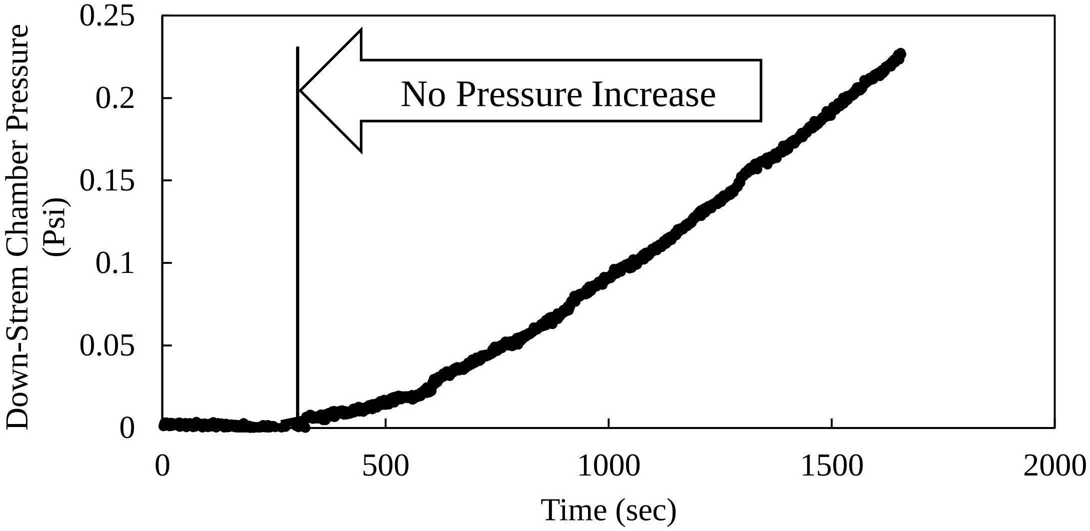


Figure 25: Non-Coated Samples Start of permeation process at 1200 Psi

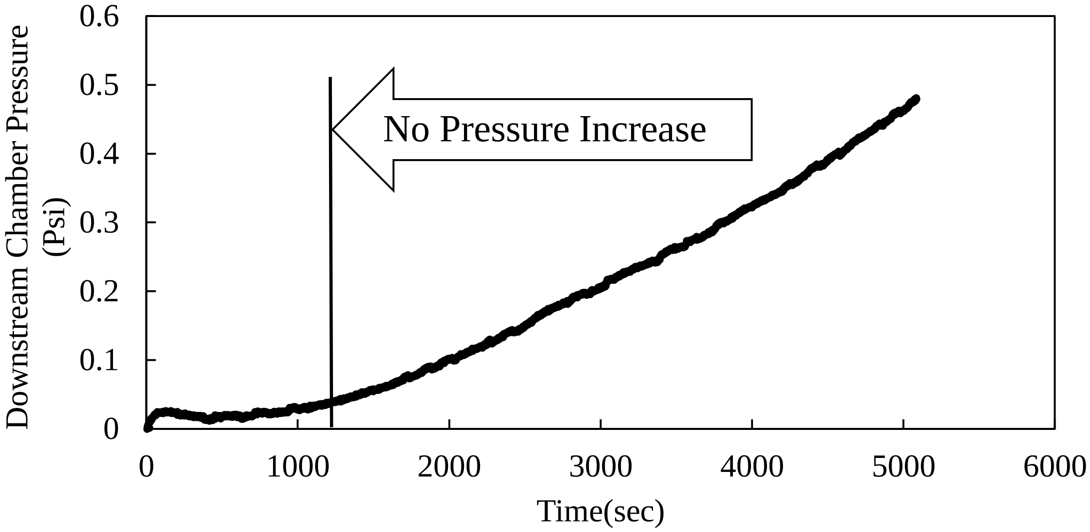


Figure 26: Coated Samples Start of permeation process at 1200 Psi

6.2.3 Soaking Membranes in Hydraulic Oil

As mentioned earlier, one of the goals of this research was to find methods for improving barrier properties of polymers which are simple enough to be applied to the polymers in a real field. Coating the polymers has been proven to be effective in decreasing the amount of gas transferring through the membranes. However, the real world condition governing a field may lead to unwanted flaws in the coatings. As it has been investigated in various studies, flaws in Nano and Macro sizes can result in drastic reduction of the coatings barrier properties.

High viscosity fluids such as hydraulic oils have high resistance to gas transfer. In such fluids, the activation energy for transferring molecules of gas is high which helps to have a slower rate of mass transfer [85]. Measuring diffusion coefficient and mass transfer rate in fluids is usually performed by a diaphragm cell or a U-tube cell [86, 87]. In the last part of the research, a practical technique was studied. This technique is used in oil and gas industry by operators in the field. The membranes are soaked in hydraulic oil for 24 hours before being employed as barriers.

6.2.3.1 Material and Sample Preparation

Hydraulic oils are available in all fields and can be easily added to a polymeric protective packaging. Therefore, a hydraulic oil was selected to be tested for the effect on gas transport and improving a packaging system barrier efficiency. Hydraulic Oil HVI 26, a commonly used hydraulic oil was selected for testing. The Viton(R) rubber sheet with a hardness of 70 Durometer was used for testing. It was purchased from E. James Company.

Polymeric membranes were cleaned by an alcoholic base cleaner and stored in moisture proof bags.

6.2.3.2 Experimental Results

In the suggested barrier system, the free volume of the polymer can be filled with the hydraulic oil. It can be assumed that the transfer of gas molecules happens through two different phases, solid and fluid. Therefore, it is expected to observe lower permeation rates compared to non-soaked materials. All the experiment were performed at a pressure of 1200 Psi and two levels of temperature, 30˚C, and 75˚C. The permeation results are displayed in Figure 27.

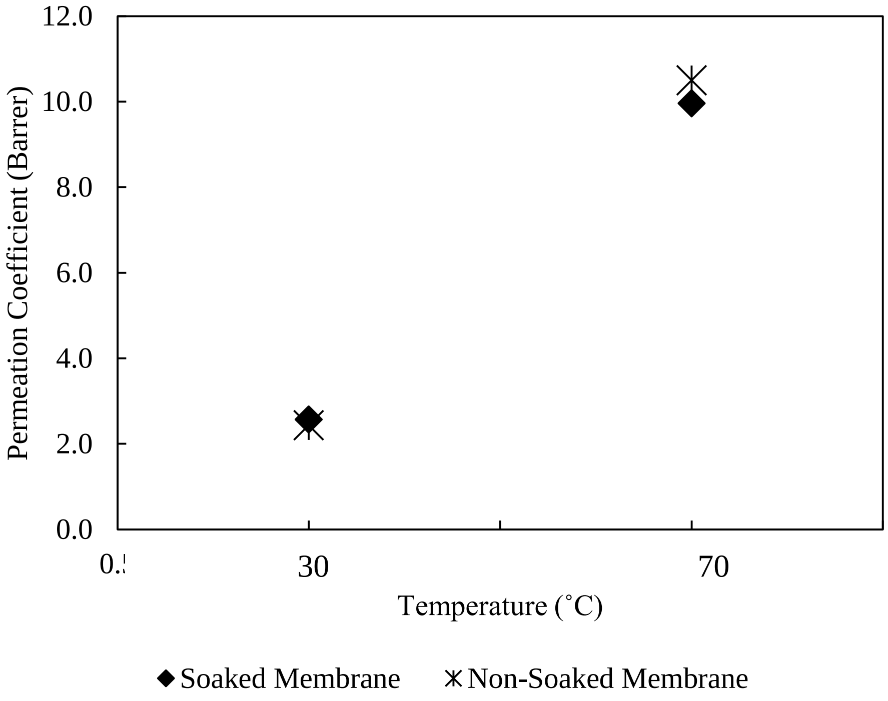
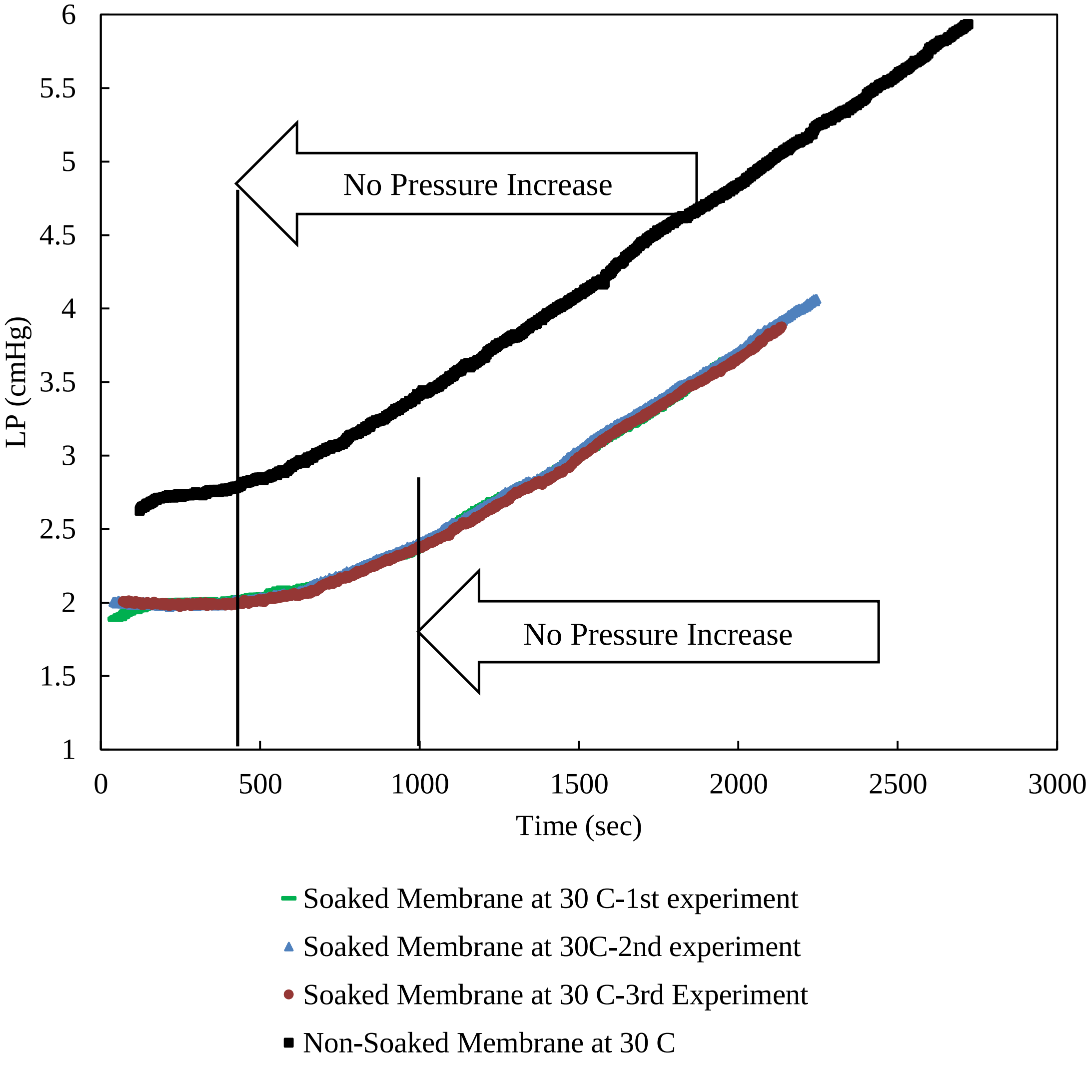
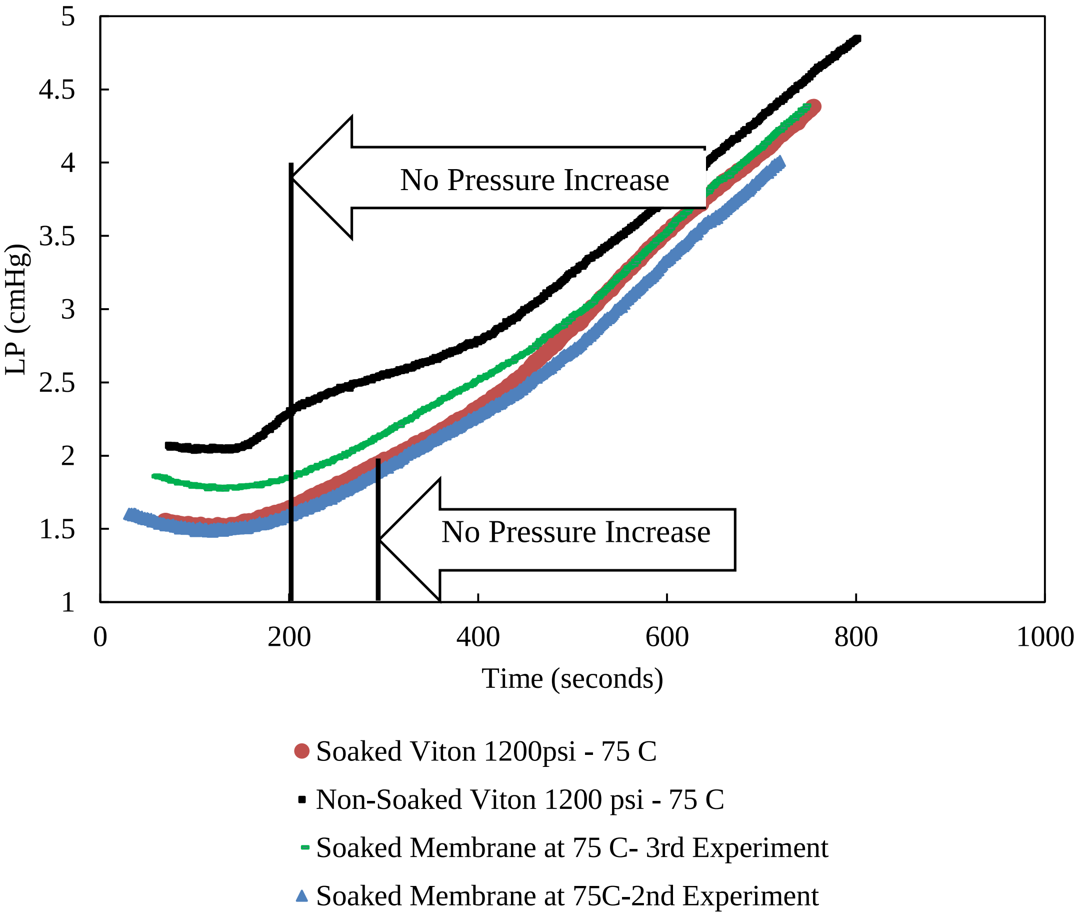


Figure 27: Gas permeation in Soaked Membrane versus Non-Soaked Membranes


6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
LP (cmHg)
0
500
1000
1500
2000
2500
3000
Time (sec)
No Pressure Increase
No Pressure Increase
Soaked Membrane at 30 C-1st experiment
Soaked Membrane at 30C-2nd experiment
Soaked Membrane at 30 C-3rd Experiment
Non-Soaked Membrane at 30 C

(a)



(b)

Figure 28: Effect of soaking membranes on stalling permeation process at a) 30˚C b) 75˚C

As it is illustrated in Figure 27, the permeation coefficients for both soaked and non-soaked samples were similar at high and low temperature conditions. Soaking the membranes had an insignificant effect on the permeation coefficient. The trends of the change in the permeation are similar in both membranes. However, as it is displayed in Figure 28 soaking membranes in hydraulic oil was successful in stalling the permeation process. The stalling effect was more significant at low temperature. The starting time of permeation process increased by almost 100%. At 75˚C, soaking membrane helped in reduction the starting time of permeation process, but it was not as efficient as low temperature condition.

6.3 Summary of Chapter

Gas transfer in barriers can be reduced using various methods. Three different methods were investigated in order to find an applicable method for real world condition. In the first two methods, polymeric membranes were coated with three different type of coatings. Silicone elastomeric, silicone elastomeric with added micro sized particles, and paint were selected as the coating material.

The improvement obtained by using silicon coating was different for two polymers. It was helpful in reducing permeation in Viton (L) by 50 % while the reduction in gas permeation of Viton rubber sheets was smaller. Adding particles to the silicone coating led to a better improvement, especially at high pressure and higher temperature conditions.

High temperature resistant painting was used as the third coating. Although the results showed insignificant barrier enhancement. However, coating samples by paint led to stalling the permeation process for a longer period of time which can be helpful for short-term applications.

In addition to coating, a new method for reducing the gas transfer rate through barrier was studied. The membranes were soaked in hydraulic oil for 24 hours before permeation experiments were performed. Soaking the membranes did not have any effect on gas transfer rate. Although, by soaking the membrane the start of permeation process was stalled. By soaking the membrane the observed effect on gas permeation reduction was insignificant.

CHAPTER 7: CONCLUSIONS AND RECOMMENDATION

7.1 Conclusions

Polymeric materials are widely used as barriers against gas permeation. Different parameters can affect gas permeation such as membrane properties like the free volume available in a polymer, the size of the gas molecules and its chemistry and the temperature. Effective parameters can be identified by performing experiments.

The current study, three research questions were proposed to examine gas permeation in polymers used in the oil and gas industry as barriers. The research questions were examined through performing permeation experiments. The respective contributions as related to the gas permeation are listed in this section.

7.1.1 Research Question 1: How temperature and pressure affect gas permeation?

Several experiments were performed in order to investigate the effect of temperature and pressure on polymers.

- By performing permeation tests over a wide range of temperature (30˚C to 105˚C) a significant increase in gas permeation was observed. As it was explained in section 4.2.2, at low pressure condition (500 Psi) the permeation coefficient increased from 2.61 at 30˚C to 31.3 at 105˚C. The permeation changed in a similar way at high pressure condition (1200 Psi) from 2.44 at 30˚C to 31.82 at 105˚C. Various researchers tried to explain the permeation behavior at high-temperature conditions by the change in the size of the gas molecules, change in the solution and diffusion processes or the change in the fractional free volume of the polymer. The most common theory is the increase in the free volume of the polymer at higher temperatures. Increasing temperature leads to relaxation of the packing in the polymer chains which leads to increasing free volume in the polymer. Therefore, the rate of gas transfer increases through a higher free volume in the polymer.

- The study about pressure was performed on two different Viton polymers. One of the Viton polymers was purchased commercially, Viton (R), and the other one was supplied by an oil and gas company, Viton (L). As the results plotted in section 4.3.2 shows both materials showed insignificant change due to change in pressure from 100 Psi to 1200 Psi. Although the same permeation behavior pattern was observed in both materials. Maximum in permeation was observed around 400 Psi. The permeation continued to reduction a minimum was observed at 1000 Psi. The difference between maximum and minimum was 13% for Viton (H) and 18% in Viton (R). The reason behind changing the permeation behavior of the two polymers may be due to the dissimilarity of the pressure effect on the solubility and diffusion process. Increasing pressure results in a reduction of diffusion due to compacting of the polymer chains. While according to Henry’s law, solubility increases at higher pressures. Therefore, based on the pressure acting on a polymeric membrane, different behavior can be observed in permeation.

7.1.2 Research Question 2: Is there any reliable model to predict gas permeation?

By observations made in the previous section of the research, the temperature was recognized as a parameter affecting gas permeation significantly. In the second part of the research, experimental results were used to obtain a prediction tool.

- An Arrhenius relationship was employed to model permeation as a function of absolute temperature. The model was successful in predicting permeation at other pressures. Testing model for prediction permeation at a different pressure showed small errors. Therefore the obtained equations in section 5.3 can be used to predict gas permeation for the conditions where no experimental data exist.
- The obtained Arrhenius relationship also was helpful in the estimation of the activation energy required for gas permeation through Viton. As it was reported in Table 5, the average value of estimated activation energy needed for Helium permeation through Viton (R) was 7.4665 Kcal/mole.

7.1.3 Research Question 3: What are the applicable methods for enhancing gas barrier properties of the existing barriers?

In this part of the research, a literature review was conducted to identify the existing methods for improving barrier properties of the materials. The two most common barrier improvement methods are embedding Nanoparticles in the polymer structure and applying a coating on the surface of the material. The main goal of this research was to reduce the permeation in the packaging materials of equipment which already is installed in the field.

Therefore, different types of the surface coatings were selected to be applied in order to enhance barrier properties of the membranes.

- In the first set of experiments, polymeric membranes were coated by silicone elastomeric material. Experiments were performed on two types of Viton, one purchased commercially, Viton B, and the other one supplied by an oil and gas company, Viton (L). As it is explained in section 6.2.1.2, applying an elastomeric coating on Viton (L) resulted in more than 50% improvement. However, the improvement in Viton B rubber sheet was in the range of 10% to 20% which is significantly smaller. This observation can be due to inefficient bonding between the Viton B and the elastomeric coating.
- Embedding Nanoparticles was one of the methods for improving gas barrier properties of the material. Therefore, Nanoparticles were added to the elastomeric coating in the second set of coating experiments. Adding clay particles resulted in barrier properties improvement. The permeation reduction was more significant at higher pressures and high temperature conditions. As the obtained results showed in section 6.2.1.2, at 500 Psi adding particles led to a 5% improvement at 30˚C and 75˚C, but the obtained improvement at 100˚C was 28.3%. The improvement observed at 1200 Psi was more significant. At 1200 Psi, adding particles led to a 30% improvement at 30˚C and a 50% improvement at 75˚C; the maximum improvement obtained at 100˚C, by the value of 64%. Adding particles to the coating may reduce the free volume of the coating. As mentioned before, reduction in the free volume of a material leads to a reduction in gas permeation. The

conclusion in the first part of the research stated that the free volume of the material decreases with increasing pressure. Therefore, this greater improvement in barrier properties at higher pressures can be considered as an evidence for the theory suggested in the first part of the research.

- In the third set of coating experiments, high temperature resistant paint was applied as a surface coating. The effect of paint coating on improving barrier properties was insignificant. The average reduction of permeation was 5%. The maximum improvement was observed at 500 psi and 100˚C. An interesting result of applying paint as the coating was stalling the permeation process. As it is shown in section 6.2.2, for a non-coated membrane the average time of starting the permeation process is almost 400 seconds, which is increased to 1200 seconds by applying paint coating. This observation can be applicable in short term protection problems.
- In the last set of barrier enhancement experiments, a practical method used in oil and gas fields by operators was examined. Membranes were soaked in the hydraulic oil for 24 hours before performing permeation experiments. Soaking membranes had no significant effect on the rate of gas transfer. However, the start of permeation experiments in soaked-membranes was delayed compared to non-soaked membranes. Soaking membranes was helpful in installing the permeation process particularly in low-temperature condition which can be applied in short term permeation problems. At low temperature permeation in non-soaked membranes started at 450 seconds compared to 1000 seconds for the soaked membrane. In the

high pressure condition, the stalling effect was not that significant, permeation started at 250 seconds for soaked membranes compared to 150 for non-soaked membranes.

7.2 Research Limitations and Challenges

Performing experimental research requires a lot of time and money in most cases which can turn into the restrictions of the research. One of the most challenging issues in this research was performing experiments at high temperature and high-pressure conditions. All the equipment such as sensors, valves, tubing, and fittings should have been capable of working in extreme temperatures and pressures condition. Therefore, the experiments range was limited by the operating range of the available equipment.

Other limitations involved the shortage on the samples provided from oil and gas industry. Therefore, the resources should have been used efficiently.

7.3 Recommendations

For the future of this research, following points can be considered:

- Employing a vacuum pump and connecting it to both upstream and downstream sides of the permeation cell. Adding a vacuum pump to the system can make the procedure of sample preparation easier. In the current procedure, the samples are placed in the vacuum oven before the tests for half an hour in order to remove the moisture and then stored in moisture proof bags. Therefore, a part of sample preparation can be performed after assembling test set-up. Vacuuming the sample after the assembly of set-up can remove any moisture absorbed in the sample during the assembling process. At the same time, both gas chambers purge and any gases other than the test gas will be removed.

- Coating samples with elastomeric material with added Nanoparticles showed successful results in enhancing barrier properties. Preparing the coating is an elaborate procedure that needs to be performed in controlled conditions by skilled operators. Therefore, research can be conducted to find an elastomeric coating material that can be prepared and applied in a simpler way. Finding a coating that can be sprayed on the samples and has a shorter curing time at room temperature is preferable. A proper start point for this research can be the material used as binders in paint industries. Combinations of different pigments and impermeable Nanoparticles can be added to the binder to create a low permeation paint coating.

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