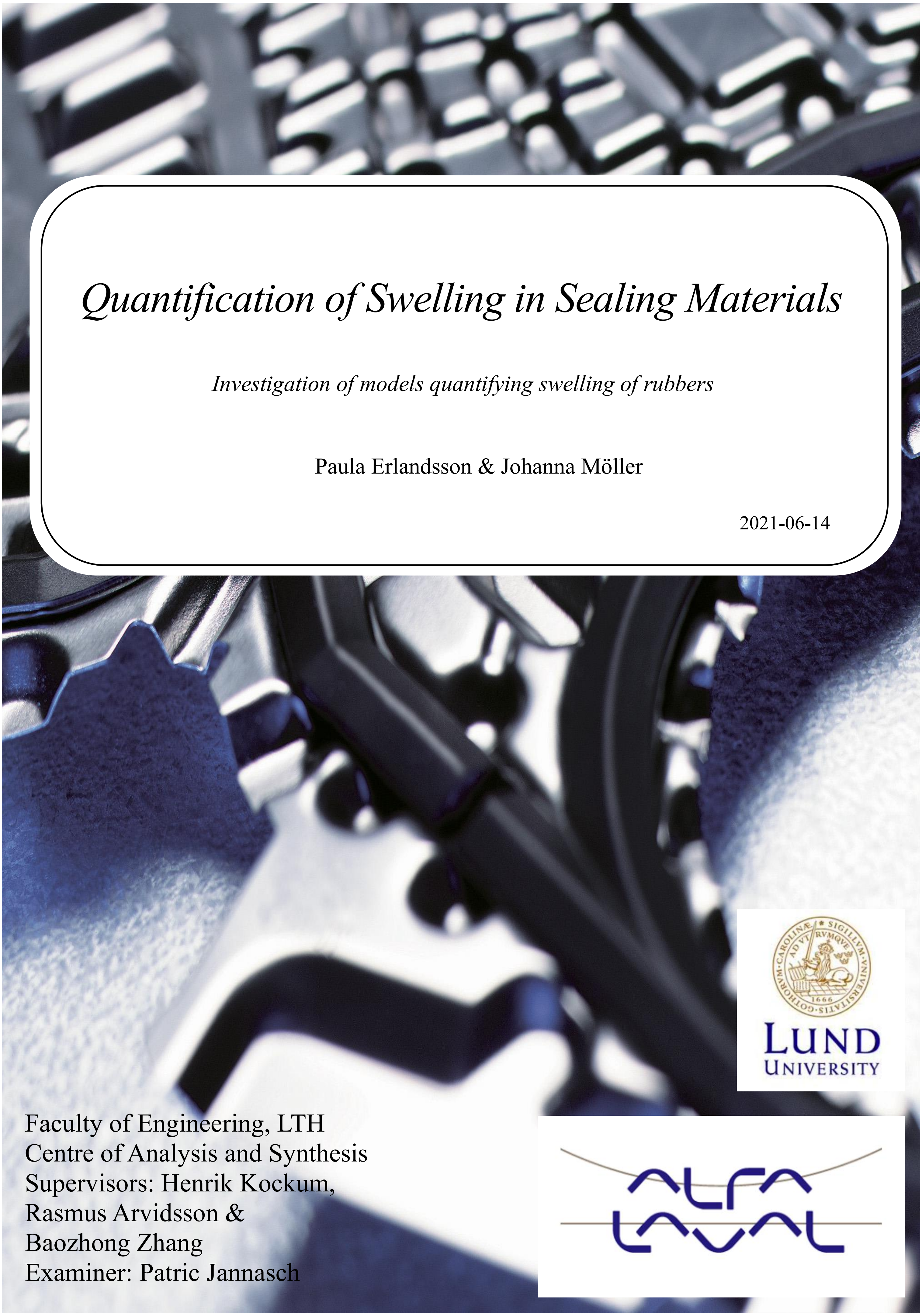


Quantification of Swelling in Sealing Materials

Investigation of models quantifying swelling of rubbers

Paula Erlandsson & Johanna Möller

2021-06-14

Faculty of Engineering, LTH
Centre of Analysis and Synthesis
Supervisors: Henrik Kockum,
Rasmus Arvidsson &
Baozhong Zhang
Examiner: Patric Jannasch

Abstract

The objective of this study was to quantify swelling in gasket materials to better predict the gaskets life span in heat exchangers. Alfa Laval produces plate heat exchangers, which are a common unit within the process industry. There are different types of plate heat exchangers, and one type is sealed with gaskets. Two common types of rubber used as gasket materials are EPDM and NBR which are studied in this report. A problem that can occur in gasketed plate heat exchangers is that the gasket swell, due to a lack of resistance from the selected gasket material toward the medium. The swelling increase can cause the gaskets to be nonreusable after opening and cleaning the heat exchanger, as it no longer fits. It can also result in failures with leakages.

Both types of rubber were swelled in 1-octanol and 1-decanol. Additionally, EPDM was also swelled in pentadecane and oleic acid, NBR was also swelled in triethyl citrate. The swelling was examined in two different tests, free swelling, and rubber strands. In the free swelling test, small pieces of rubber were completely immersed in a solvent. The rubber strands had only one end of the strand immersed in a solvent. This allowed solvent to diffuse up through the strand.

From the free swelling test, it was shown that most combinations displayed Fickian diffusion, with some deviations. A linear relationship was found between the diffusivity, temperature, and solvents. Similarly, a linear relationship was also found for the equilibrium swelling level, temperature, and solvent. The diffusion up through rubber strands proved to be slow. Therefore, it was examined whether it was possible to find a relationship between the diffusion distance in the rubber strands and the diffusion constant calculated from free swelling.

Sammanfattning

Syftet med denna studie var att kvantifiera svällning i packningsmaterial för att bättre förutse packningens livstid i en plattvärmeväxlare. Alfa Laval producerar plattvärmeväxlare som är en vanlig enhet i processindustrin. Det finns olika typer av plattvärmeväxlare och en typ är tätad med packningar. Två vanliga gummityper som används är EPDM och NBR som undersöktes i denna studie. Ett problem som kan uppkomma i packningsförsedda värmeväxlare är att packningen sväller, på grund av att valt packningsmaterial inte är resistent mot mediet. Svällningen kan leda till att packningarna inte går att återanvända efter öppning och tvätt av värmeväxlaren då de inte längre passar. Det kan också leda till allvarliga haverier med läckage.

Båda gummityperna svälldes i 1-octanol och 1-decanol. Utöver det så svälldes EPDM även i pentadekan och oleinsyra, samt NBR i trietylcitrat. Svällningen undersöktes med två olika test. Det första testet var med fri svällning där små gummibitar var helt täckta i vätska. Det andra testet var med remsor där ena änden av remsan var neddoppad i vätska. Detta möjliggjorde att vätska kunde diffundera upp genom remsan.

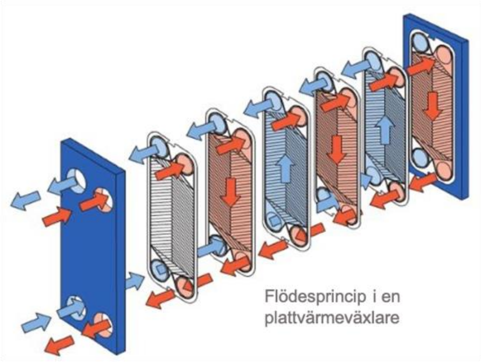
Från de fria svällningsförsöken visade det sig att Ficksk diffusion gällde, men med några avvikelser. Ett linjärt samband hittades mellan diffusionskonstanten, temperatur och lösningsmedlet. Ett liknande linjärt samband hittades för svällningsjämviktsvärdet, temperatur och lösningsmedlet. Diffusionen upp genom gummiremsor visade sig vara mycket långsam. Därför undersöktes det om ett samband kunde identifieras mellan diffusionlängden i remsorna och diffusionkonstanten beräknad från fri svällning.

Populärvetenskaplig sammanfattning

Gummiband, studsbollar, suddgummi och bildäck är några exempel på saker som man troligen stött på någon gång i vardagen och som är gjorda av gummi. Det går inte att förneka att gummi har en stor betydelse för hur vi lever idag, allt från föremålen vi stöter på i vardagen till tätningar i processindustrin. När gummi tar upp (absorberar) vätska så sväller det, detta fenomen kallas svällning. Svällning är en oerhört viktig del för att kunna bestämma gummits hållbarhet och lämplighet vid olika typer av applikationer. Därav var målet med detta projekt att bättre förstå och förutse svällning i gummi.

Gummi har unika egenskaper som gör att tex. en studsboll studsar tillbaka till dig. Andra användningsområden som gummits unika egenskaper passar till är t.ex. inom tätning. Vanliga tätningsapplikationer är dammbottnar, underjordiska tunnlar, dörrar, fönster, värmeväxlare, med mera. Gummi fungerar bra som tätning för att det kan återfå sin form efter att man har deformerat det. Ett vardagligt exempel på detta är att ett gummiband snärtar tillbaka efter att man har dragit ut och släppt det. Andra egenskaper som är intressanta är att gummi kan ta upp lösningsmedel utan att lösas upp. När gummi tar upp lösningsmedel ökar volymen. Detta kallas svällning. Svällning kan både vara positivt och negativt beroende på applikationen. I underjordiska tunnlar är det önskvärt att gummipackningar sväller, i värmeväxlare är det däremot negativt då svällning kan orsaka haverier.

Alfa Laval ligger i framkant vad det gäller tillverkning av värmeväxlare. Användningsområdet för en värmeväxlare är brett, allt i från livsmedelsindustrin till oljeindustrin. En värmeväxlare används för att överföra energi i form av värme mellan två vätskor utan att vätskorna blandas. I en plattvärmeväxlare sitter plattor tätpackade intill varandra. Värmeöverföringen sker då mellan plattorna. Hur en plattvärmeväxlare är uppbyggd och hur vätskor flödar i den visas i bilden nedan.



För att hålla vätskorna isär och för att värmeväxlaren inte ska läcka använder man tätningar som oftast består av gummi. Att gummi sväller kan orsaka problem i en värmeväxlare, så som att en packning blir för stor för att passa i värmeväxlaren vilket kan leda till läckage och att packningen behöver bytas. Därför är det av stor vikt att kunna förutse hur mycket och snabbt en packning sväller.

Detta projekt syftade till att skapa matematiska modeller som kan hjälpa Alfa Laval att förutspå inte bara *om* gummi kommer att svälla och hur mycket i ett visst lösningsmedel, utan också vid vilka temperaturer, samt hur snabbt. Resultaten i detta projekt visar att det är möjligt att hitta matematiska modeller som förutser svällning. Det har även presenterats ett tillvägagångssätt för att kunna ta fram liknade modeller för andra kombinationer av gummi och lösningsmedel än de som har testats i vårt projekt. Dessa modeller kan Alfa Laval eventuellt använda i framtiden för att t.ex. ta reda på hur olika gummi kommer att påverkas av en temperaturförändring och hur lång tid det kommer att ta för ett gummi att svälla i ett visst lösningsmedel.

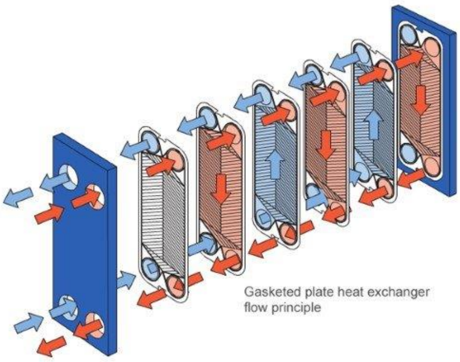
Utöver detta har andra oväntade och intressanta resultat dykt upp, bland annat, att den maximala svällningen inte alltid ökar med temperaturen (det normala är att svällning ökar med temperaturen) vilket troligen beror på vilken typ av interaktioner som verkar mellan gummit och svällningsmedlet.

Popular abstract

Rubber bands, bouncing balls, erasers and car tires are some examples of things that you probably have encountered at some point in everyday life that are made of rubber. There is no denying that rubber is of great importance to how we live today, involving everything from the objects we encounter in our everyday life to seals in the process industry. Rubber can absorb liquids and increase in size without dissolving. This phenomenon is called swelling. Swelling is a crucial part of determining the durability and suitability of the rubber in different types of applications. Therefore, the goal of this project was to better understand and predict swelling in rubber.

Rubbers have unique properties that make e.g. a bouncing ball bounces back to you. Other applications that the rubber's unique properties are suitable for are e.g. sealing materials. Common sealing applications are important for underground tunnels, doors, windows, heat exchangers, and many more. Rubber works well as a seal as it can regain its shape after it has been deformed. An example of this is that a rubber band snaps back after you have pulled it out and released it. As mentioned, another unique property is that rubber can absorb solvents without dissolving. When rubber absorbs solvents, the size increases. This is called swelling. Swelling can be both positive and negative depending on the application. In underground tunnels, it is desirable for the gaskets to swell. However, in heat exchangers, swelling is not desired since it can cause failures

Alfa Laval is at the forefront of manufacturing heat exchangers. The field of application for a heat exchanger is large, everything from the food industry to the oil industry. A heat exchanger is used to transfer energy in the form of heat between two liquids without mixing the liquids. In a plate heat exchanger, plates are tightly packed next to each other. The heat transfer then takes place between the plates. How a plate heat exchanger is constructed and the liquids flow thorough the exchanger can be seen in the picture below.



Seals are used to keep the liquids apart and to prevent the heat exchanger from leaking. The seals usually consist of rubber. If the rubber seal swells it can cause problems in a heat exchanger. One of these problems is that gasket becoming too large to fit in the heat exchanger, which can lead to leakage and the gasket needing to be replaced. Therefore, it is of great importance to be able to predict how much and quickly a gasket swells.

This project aimed to create mathematical models that can help Alfa Laval predict not only whether rubber will swell and how much in a given solvent, but also at what temperatures, and how fast. The results of this project show that it is possible to find mathematical models that predict swelling. An approach has also been presented to be able to develop similar models for other combinations of rubber and solvents than those that have been tested in our project. Alfa Laval may use these models in the future to e.g. to find how different rubbers will be affected by a temperature change and how long it will take for rubber to swell in a certain solvent.

In addition to this, other unexpected and interesting results were obtained. For example, the maximum swelling does not always increase with temperature (it is normal for swelling to increase with increasing temperature), which probably depends on the type of interactions between the rubber and the swelling liquid.

Acknowledgements

Thanks to Alfa Laval for giving us the opportunity to carry out our thesis work here and providing us with all the necessary materials, equipment, and knowledge.

We would like to thank our supervisor at Alfa Laval, Rasmus Arvidsson and Henrik Kockum for all the guidance and interesting discussions during the entire project. An additional thanks to Stefan Olausson for participating in the discussions and for always being available for guidance in the lab.

We would also like to thank our supervisor Baozhong Zhang, examinator Patric Jannasch and PhD student Hannes Nederstedt for their guidance and knowledge as well as valuable discussions.

Table of contents

1 Introduction

1.1 Background

Alfa Laval has been developing and producing heat exchangers since 1938. At Alfa Laval’s production site in Lund, mainly gasket plate heat exchangers are produced. In the gasketed plate heat exchanger, sealing materials, made of rubber, are used to seal between the fluids and the surrounding. Two of the sealing materials that are currently used by Alfa Laval are ethylene propylene diene rubber (EDPM) and nitrile rubber (NBR). Rubbers are polymeric material and can therefore swell. Swelling means that the material increases in volume and this occurs when the solubility of a fluid matches the solubility of the rubber making the liquid diffuse into the rubber. The swelling can increase the degradation and chain scission effect of the rubber. Alfa Laval has identified a need to expand their knowledge in swelling to be able to better predict the expected lifespan of the sealing material. Hence, the motivation of the project is to gain a deeper understanding of how swelling of sealing materials is affected by different parameters, such as time, temperature, and process fluid.

1.2 Scope

The scope of this project was to develop a model for swelling as a function of temperature, contact time, diffusion rate, and diffusion distance as well as to formulate a method how to collect necessary data to apply the model for any combination of fluids and rubbers.

2 Theory

2.1 Heat exchanger

Heat exchangers are a common device in many different types of industries, ranging from refineries to the food industry. Heat exchangers are used to transfer heat from one fluid to another without mixing the two fluids. This is an energy-efficient process, as residual heat from a hot stream can be used to pre-heat an incoming fluid. [1]

Alfa Laval offers a variety of heat transfer solutions, including heat exchangers. Different types of heat exchangers are produced by Alfa Laval including, plate heat exchanger and tubular heat exchanger. Moreover, the plate heat exchanger can be divided into various categories. One of these categories is the gasketed plate heat exchanger. Other categories include brazed heat exchangers and more. The gasketed heat exchanger can be seen in Figure 1. [1]

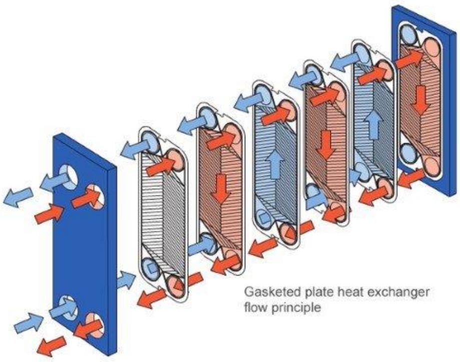


Figure 1. Schematic overview of a gasketed plate heat exchanger. With courtesy to Alfa Laval.[1]

Uniquely to the gasket plate heat exchanger, the channels are sealed by placing a rubber gasket in-between each plate. This allows opening which is not possible when the channels are sealed by brazing. The gasketed plate heat exchanger is preferred in applications, where opening the heat exchanger to clean the plates is important, e.g., in the food industry. The gaskets are often made from rubber. An image of a gasket is shown in Figure 2. Two common rubber material types used by Alfa Laval are EPDM and NBR, which are the rubber materials investigated in this study. [1]

Figure 2. The left image shows a corner of a plate with a gasket. The right image shows different types of cross-sections of a gasket.

2.2 Rubber

The first discovered rubber was latex, a.k.a. natural rubber, which comes from the tree Hevea Braziliensis. The people of Mesoamerica were the first humans to extract the rubber from the milky fluid in the trees and they utilized the rubber already 1700 B.C. They made the rubber into balls, sole for shoes, etc. [2],[3] The unique properties of latex made it popular and today there are many synthetic materials with similar properties. Rubber is a collective name for all materials with similar properties to natural rubber and is also called elastomer. [4]

Rubber is a mixture of several ingredients, and each type of rubber has a unique composition. The key components of rubber are the polymers and the vulcanizing agent, but can also include additives such as carbon black, chalk, glass fibres, plasticizers, and antioxidants. The purpose of the vulcanization agent is to form the crosslinked network which gives the rubber its elastomeric properties. Depending on the mixture, the properties of the rubber changes. Even rubbers with the same type of polymer can have different properties depending on, e.g., the crosslink density and amount of filler. [3], [5]

Elastomers can either have properties of thermosets or thermoplastics. The difference between thermosets and thermoplastics is that thermosets have a crosslinked network while thermoplastics are not connected by chemical bonds. Instead, thermoplastics obtained their elastomeric properties by crystalline or hard glassy domains. The difference makes thermoplastics reprocessable since they can be dissolved in appropriate solvents and melted upon heating. Moreover, thermosets are not possible to reprocess by heat since they would degrade instead of melt. EPDM and NBR that are studied in this project are thermosets. [5]

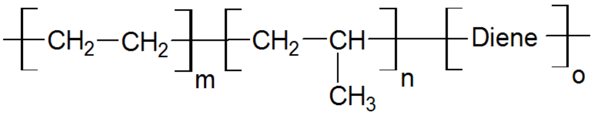
One of the unique properties of rubber is the ability to get highly deformed at the cost of a small stress, i.e., rubbers are soft. Rubbers also have unique thermoelastic properties, when stretching a rubber under a constant load, it emits heat. Likewise, a stretched rubber contracts if heated. This is known as the Gough-Joule effect. [4]

The properties of rubber can change due to strain (physical relaxation), temperature change, scission of crosslinks due to chemical reactions (chemical relaxation), swelling (see section 2.5), etc. The rubber’s ability to recover after a compressive force is measured as a compression set, which is a measurement of the remaining deformation of the rubber after the compressive force is removed. [6]

For a rubber to be suitable as a gasket in a heat exchanger it needs to have low compression set since the function of the gasket is to provide a high sealing force and maintain its shape over a long time. Also, the gasket needs to withstand the process temperature, the warm and cold stream which exchanges heat.

2.3 EPDM

Ethylene propylene diene rubber (EPDM) is a synthetic rubber that consists of ethylene, propylene and a small amount of diene, see Figure 3. Dienes have double bonds, which makes sulphur vulcanization possible for the polymer. The double bonds are located at the side chain; hence, the backbone is saturated making the rubber resistant against ozone, heat, and light. The rubber can be used in temperatures ranging from – 35 °C to 125 °C, even higher if vulcanized with peroxide. Peroxide vulcanization also gives better setting properties compared to vulcanization with sulphur, overall EPDM has a low compression set. [3]



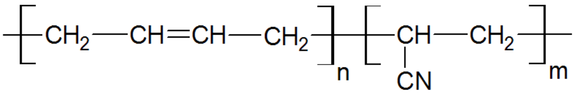
$$-\left[CH_2-CH_2\right]_m\left[CH_2-\underset{CH_3}{CH}\right]_n\left[\text{Diene}\right]_o-$$

Figure 3. Structure of EPDM. With courtesy to polymerdatabase.com. [7]

EPDM is a non-polar rubber. Therefore, EPDM is highly resistant against water and other polar fluids and not resistant against non-polar fluids as oil. Like other rubbers the recipe of EPDM determine the exact properties, for example, the diene content determines the rate of vulcanization. EPDM is a suitable sealing material for many processes since it is resistant to warm water, vapour, and oxidative chemicals. Except for being used as a sealing material in heat exchangers, it is used for sealing windows and doors in buildings, but it can also be used to make cables and much more. [3]

2.4 NBR

Nitrile-butadiene rubber (NBR) is a synthetic rubber consisting of a copolymer of butadiene and acrylonitrile, see Figure 4. NBR can be used in the temperature range of –40 °C to 90 °C. NBR can be vulcanized with both sulphur and peroxide. Similarly to EPDM, vulcanization with peroxide decreases the compressive set and increase the thermal stability up to 100°C. [3]



$$-\left[CH_2-CH=CH-CH_2\right]_n\left[\underset{CN}{CH}-CH_2\right]_m-$$

Figure 4. Structure of NBR after 1,4 addition. With courtesy to polymerdatabse.com. [8]

As mention for EPDM, the exact properties of an NBR rubber depends on the recipe. NBR is more polar than EPDM and therefore has a higher oil resistance but has a lower resistance for polar substances such as esters. NBR also has high resistance against water but slightly less compared to EPDM. The backbone of NBR includes double bonds which makes NBR more susceptible to degradation from ozone, heat and light than EPDM. Just as EPDM, NBR has a wide range of industrial uses, including, sealing materials, membranes, O-rings, and many more. [3]

2.5 Swelling of rubbers

The process of fluids absorbing and dissolving in rubber is called swelling. The swelling ratio can be defined either by mass, molar, or volume percentage. In this project, the swelling, Q, has been defined as the weight percentage as shown in equation (1).

$$Q = \frac{m_t - m_0}{m_0} \cdot 100\ \% \tag{1}$$

Where m_t is the weight of the test piece after t days and m_0 is the starting weight. In equation (1), the volume change that can occur during mass uptake is not explained. For a swelled polymer, the swelling volume ratio, Q_v can be calculated from the weight change with equation (2). [9]

$$Q_v = 1 + \left(\frac{m_t}{m_0} - 1\right)\frac{\rho_p}{\rho_s} = 1 + Q\,\frac{\rho_p}{\rho_s} \tag{2}$$

Where ρ_p is the density of the unswollen polymer and ρ_s is the density of the pure solvent. [9] Even though the volume increase is the factor that causes failures in a heat exchanger, it has been chosen to work with masses since the mass and volume ratio are related as can be seen in equation (2). Also, the measurement of mass is simpler and more precise.

There are two suggested swelling mechanisms depending on whether the swelling liquid is water or carbon-based. The first one is osmosis based which occurs when water is the swelling medium. The second one is adsorption/diffusion-based, where the fluid diffuse to the surface and adheres to it. Then the liquid will diffuse through the surface and then in the rubber. [10], [11]

Rubber can have a high degree of swelling since it does not dissolve due to the cross-linked network. The driving force for everything, including swelling, is to minimize Gibbs free energy. Spontaneous reactions occur if the Gibbs free energy is negative. As the rubber swells, the swelling medium takes up space and the rubber get stretched (the polymer chains get elongated), which leads to a decrease in entropy, which counteracts swelling. The main driving force for swelling is the entropy of mixing, which is positive. [12]

Polymer solutions are usually entropic, and the entropy of mixing can be calculated from the Flory–Huggins solution theory. Flory–Huggins solution theory is derived from a lattice model that considers the size difference between the solvent and the polymer. The enthalpy of mixing can also be calculated with this theory. To calculate the enthalpy an interaction parameter (χ) is used. Since a crosslinked polymer does not get dissolved as mentioned above, the theory is not valid for crosslinked polymers. Flory–Rehner Theory of polymer network swelling is instead used for describing the thermodynamics of rubber and solvent solutions. This theory used the Flory–Huggins solution theory to calculate the free energy of mixing and includes another term for the elongation of the rubber that occurs when the rubber swells. [12]

Many factors influence the degree of swelling, e.g., temperature, pressure, time, interaction forces and the molar volume of the solvent. [13]. The swelling process of rubber that experiences compressive strains is initially not affected by the pressure. [14] However, after long exposure times, the swelling equilibrium decreases with applied compression pressure because the rubber has only the possibility to expand in one or two directions. [14], [15] The swelling rate is also affected by parameters such as temperature, molecular size, as well as the geometry of the rubber. [16], [17]

Swelling affects the properties of the rubber in many ways. The changes depend mainly on the swelling medium and the degree of swelling. Swelling can, e.g., increase chain scission, decrease the elastic modulus and soften the rubber. [11], [18] This can cause severe problems in applications such as sealing materials in heat exchangers as the heat exchangers start to leak or that the gasket does not fit due to the volume change.

2.6 The Cohesive Energy and Hansen Solubility Parameters

The cohesive energy (E_{coh}) of a substance in the liquid or solid-state is the energy needed to eliminate all intermolecular forces. For a liquid of low molecular weight, the cohesive energy can be calculated from the enthalpy of vaporization. A polymer decomposes before it vaporizes, therefore the cohesive energy of a polymer is calculated by group contribution but there are also other methods. Another method is to find the solvent, with known parameters, that maximizes the swelling in the polymer. The polymer is then assumed to have the same value as the solvent. [19], [20]

The cohesive energy density is obtained if dividing the cohesive energy with the volume, and the square root of the cohesive energy density gives the solubility parameter (δ), see equation (3), which has the dimension pressure$^{1/2}$.

$$\delta = \sqrt{\frac{E_{och}}{V}} \tag{3}$$

By comparing the solubility parameter for a polymer and a solvent, their compatibility can be estimated. As “like dissolves like”, the general rule is that the polymer and the solvent will be more soluble the more similar solubility parameters they have. This solubility parameter is also used as an indicator to determine the resistance of rubber against a solvent. [19]

Hansen’s solubility parameters are a further development of the solubility parameter. Hansen’s solubility parameters are divided into the three main intramolecular forces: hydrogen bonding (δ_h), dispersive forces (δ_d), and polar forces (δ_p). The relationship between Hansen’s solubility parameter and the solubility parameter is described in equation (4). [19], [21]

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{4}$$

These three parameters predict the solubility of two substances by comparing the same way as for the total solubility parameter, but each Hansen’s parameter is compared individually. This leads to Hansen’s parameters predicting solubility better than the total solubility parameter. An example of this is that the total solubility parameter can be the same but have a large difference in the three different forces. Hence, the solvent and rubber will not be soluble which Hansen’s solubility parameters will predict. On the other hand, the total parameter would predict the rubber and solvent to be soluble even if they are not. Moreover, Hansen’s solubility parameters have a temperature dependence which is stated in equations, (5), (6) and (7) for liquids.

$$^{d\delta_{\mathrm{D}}}/_{dT} = 1.25\alpha\delta_D \tag{5}$$

$$^{d\delta_P}/_{dT} = 0.5\alpha\delta_P \tag{6}$$

$$d\delta_H / dT = -\delta_H(1.22 \cdot 10^{-3} + 0.5\alpha) \tag{7}$$

Where α is the thermal expansion factor of the liquid and the temperature, T, is the temperature in K. Hansen's solubility parameters for the solvent investigated in this project are seen in Table 1. The values presented in Table 1 is taken from Table A.1 in Hansen's handbook. [21]

*Table 1. Hansen's solubility parameters and molar volume for a selected set of solvents at an unknown temperature. [21] *Calculated from values found in PubChem [22].*

Solvent	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	Molar volume (cm^3/mol)
1-Octanol	16.0	5.0	11.9	157.7
1-Decanol	16.0	4.7	10.0	191.8
Triethyl citrate	16.5	4.9	12.0	243.0
Pentadecane	16.8	0.0	0.0	276.4*
Oleic acid	16.0	2.8	6.2	317.0

2.7 Diffusion

Diffusion is a random motion driven by the concentration gradient. All systems at normal conditions which are not in equilibrium are driven to minimize the concentration difference. Fick's first law explains the relationship between the diffusive flux, J, and the concentration gradient, ∇c, see equation (8). [23]

$$J = -D\nabla \mathrm{c} \tag{8}$$

D is the diffusion coefficient. For a one- dimensional system it is simplified to equation (9).

$$J = -D\frac{\partial c}{\partial x} \tag{9}$$

Where x is the spatial position. Fick's second law, also called diffusion equations, predicts how diffusion changes the concentration over time. Fick's second law for three dimensions is shown in equation (10)

$$\left(\frac{\partial c}{\partial t}\right) = D\nabla^2 \mathrm{c} \tag{10}$$

Where t, is the time. For one-dimension, it is simplified to equation (11).

$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial x^2}\right) \quad (11)$$

This is valid if D does not change with x.

If a polymer system follows Fick's diffusion depends on the polymer's relaxation time and the diffusion rate of the fluid into the polymer; in other words, how fast the polymer can adjust to the swelling media. Rubbers therefore often exhibit Fickian diffusion since they usually have a short relaxation time. On the other hand, if the polymer is stiff and has a long relaxation time it does not follow Fick's diffusion. [24]

2.8 Mathematic modelling of diffusion

There are many different mathematical models considering diffusion, including solutions for swelling and semi-infinite systems. Commonly, diffusion in a semi-infinite system means that the surface concentration is constant, and the concentration is zero at an infinite distance from the surface, leading to the boundary conditions $C=C_1$, $x=0$, $t>0$ and $C=0$, $x=h$, $t>0$ as well as the initial condition $C = C_0$, $0 \leq x \leq h$, $t=0$, for plane geometry. This gives the analytical solution to Fick's second law (equation (11)) as shown in equation (12) [24].

$$\frac{C-C_1}{C_0-C_1} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (12)$$

C is the concentration at the position x after time t. C_0 and C_1 are the initial and surface concentration of the system respectively. D is the diffusion coefficient and erf denotes the Gaussian error function. [24] For the curious reader, the definition of the Gaussian error function is explained in [25]. The physical meaning of a semi-infinite system, in the case of this study, is that liquid uptake will occur at one end of the rubber. The liquid will diffuse up through the rubber, but the liquid will not exit the rubber at the other end, i.e., the test is described later in section 3.2.2.

Crank et al. has suggested that the kinetics of vapour uptake by rubbers with a plane geometry completely surrounded by vapour can be described according to equation (12). Here it is assumed that the diffusion coefficient and that the thickness, h_0, are constant. The initial condition is, at $t=0$, for all x, $Q(t,x)=0$. The first boundary condition is, at times $t > 0$, $x = 0$, and $x = h$, $Q(t,x)=Q_{\mathrm{surf}}$. The mass uptake at the surface, Q_{surf} is assumed to be equal to the equilibrium mass uptake, Q_{eq}, i.e., $Q_{\mathrm{surf}} = Q_{\mathrm{eq}}$.[24] The second boundary condition is not clearly stated in the literature. However, the second boundary condition is likely to be: $x=h/2$, $\partial Q(t,x)/\partial x=0$.

$$Q_t \big/ Q_{eq} = 1 - \left(8 \big/ \pi^2\right) \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \exp\{-D(2m+1)^2 \pi^2 t / h_0^2\} \qquad (13)$$

In equation (13) Q_t is the swelling (mass uptake of vapour or liquid) after time, t. Equation (13) can be used to approximate diffusion in rubber during liquid uptake and when the rubber swells. At initial times and for Fickian diffusion, equation (13) can be simplified to equation (14) (e.g., chapter 10 in [24]). [24], [26]

$$\frac{Q_t}{Q_{eq}} = 4 \cdot \left(\frac{Dt}{\pi h_0^2}\right)^{1/2} \qquad (14)$$

For Fickian diffusion, equation (14) should be linear when plotting Q_t/Q_{eq} vs $t^{1/2}/h_0$ with the slope defined as in equation (15). [6], [26]–[28]

$$slope = 4 \cdot \left(\frac{D}{\pi}\right)^{1/2} \qquad (15)$$

As mentioned previously in section 2.7, diffusion of solvent in rubber is generally Fickian, but this is not true for all cases. An equation that could be used for determining the diffusion type for free swelling in rubber is shown in equation (16). [24], [26]–[28]

$$ln\left(\frac{Q_t}{Q_{eq}}\right) = ln(k) + n \cdot ln(t) \qquad (16)$$

Where k and n are constants. If the constant n is equal to 0.5, the diffusion in the rubber is Fickian. [24], [26]–[28]

Several studies have been done to investigate the diffusion type by finding n and calculated the diffusion coefficient for various combinations of rubbers and solvents. Generally, the obtained n-values ranges between 0.3 and 0.6 with diffusion coefficients ranging from 10^{-9} to 10^{-13} m^2/s. [6], [26]–[30]

3 Method

3.1 Materials

NBR-P sheets, EPDM-C sheets (-P and -C denotes specific Alfa Laval grades of rubber.), pentadecane (Thermo Fisher, 99.9 % and Sigma-Aldrich, ≤ 99 %), oleic acid (TCI, 85 %), 1-octanol (VWR, 97 %), 1-decanol (VWR, ≤ 99 %), triethyl citrate (Sigma-Aldrich, ≤ 99 %) and toluene (VWR, ≤ 99.5 %).

3.2 Laboratory work

3.2.1 Free swelling

The laboratory work consisted of two main set-ups, one for examining free swelling and the other for studying diffusion up through rubber strands. In the free swelling experiments, the effects of time, temperature and initial mass were investigated. Rubber sheets were cut into small tests pieces with a weight ranging from 0.06 to 2.5 g. The thickness of all pieces was approx. 2 mm. The test pieces were completely covered with solvent in a beaker, see Figure 5.

Figure 5. Set-up for the free swelling test. The pieces are cut into different sizes and shapes.

In this report, the term solvent has been used to denote swelling fluids. The solvents used to swell EPDM were pentadecane, oleic acid, 1-octanol, and 1-decanol. NBR was swelled in triethyl citrate, 1-octanol, and 1-decanol. Oleic acid has low thermal stability, therefore the oleic acid in 80 °C and 50 °C was replaced with a fresh batch after 1 respectively 2 days. The studied temperatures for free swelling were, 22 °C, 40 °C, 50 °C, and 80 °C. At elevated temperatures, the beaker was either covered with an aluminium lid or enclosed in an autoclave.

When collecting data, the test pieces were removed from the solvent and washed with detergent and water to remove residual solvent on the surface of the rubber pieces before weighing. After weighing, the test pieces were put back in the solvent.

For the experiments investigating the initial weight, the test pieces were cut into 30×30, 20×20, 10×10 and 5×5 mm^2. The impact of initial weight was tested for NBR in 1-octanol at 50 °C, where three replicates of each size were used. The initial weight was also tested for EPDM in oleic acid at 22 °C, where three replicates of 20×20 and 5×5 mm^2 pieces were used. One replicate was used for the 30×30 and 10×10 mm^2 pieces.

The effect on swelling with applied compressive pressure was also investigated. This was done by clamping the rubber pieces between two parallel metal plates. The distance between the plates was controlled by metal spacers of 1.6 mm which gave a deformation of 25 %, see Figure 6. The two plates were completely submerged in the solvent. This was only studied for EPDM in pentadecane. In order to determine whether the equilibrium value was reached, three setups were used, each containing three test pieces of rubbers. One of the setups was reopened and closed to check the swelling rate and if the equilibrium level was reached. The other two set-ups were opened when the first setup had reached equilibrium.

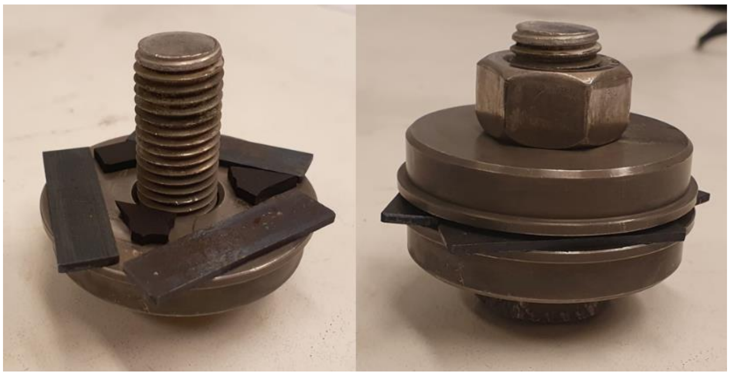


Figure 6. The equipment used to investigate the pressure on the swelling. In the left image, the upper metal plate is off to show how the spacers and the rubber pieces were placed. In the right image, the upper metal plate is on.

3.2.2 Rubber strands

The second set-up included pieces cut as long rubber strands with a thickness of approx. 2 mm, a width of 10 mm and a length in the range of 50 to 90 mm. On a distance up to approx. 50 mm, distances of 2.5 mm or 5 mm were marked by small cuts on the strands. The strands were placed approx. 10 mm down in the liquid without touching the bottom of the beaker and left for 7-30 days at 22 or 80 °C, see Figure 7 for a typical set-up.

Figure 7. Set-up for the rubber strands. The strand is placed approx. 10 mm down in the beaker without touching the bottom of the beaker.

The strands were then removed and cut into 2.5 mm or 5 mm pieces. After weighing the swelled small pieces, extraction was performed by submerging the pieces in an excess of toluene. Lids of aluminium foil were used to prevent the evaporation of toluene. After 1 day, the toluene was replaced with a fresh batch of toluene. After two days of extraction, the toluene was removed. The remaining toluene was evaporated at 80 °C for two days. Figure 8 shows the cut 2.5 mm pieces for six different strands before toluene was added for extraction. The larger pieces seen in Figure 8 is the 10 mm part that was completely submerged into the solvent.

Figure 8. Image of six strands that have been cut to be prepared for extraction.

3.3 Modelling

The collected data were analysed with Python in Jupyter notebook. The libraries NumPy, SciPy, pandas, matplotlib and sklearn were imported. For free swelling, the data were evaluated according to equation (14) and equation (16). Furthermore, the evaluation of free swelling was extended by finding a relationship between equilibrium swelling level, temperature, and solvent. The solvent's Hanson's solubility parameters and their molar volume represent the solvent in the model. Also, a relationship between the diffusion constants, temperature, and solvent was investigated. The data obtained by rubber strands were evaluated according to equation (12).

4 Result and discussion

Early in the project, it was discovered that the setup for the strands had low accuracy. The reason for this being the difficulty to define the zero level (liquid level) due to the volumetric changes as the strands absorbed solvent and because the position of the strand was difficult to obtain exactly. Hence, the zero levels differed with the time. It is of importance to accurately decide the zero levels since the diffusion distance is to be measured. Three strands that have recently been removed from the solvent are shown in Figure 9. Two of them had a vague zero level and one had a distinct zero level. It could also be observed that the strands (a) and (b) probably had been positioned further down than 10 mm in the solvent.

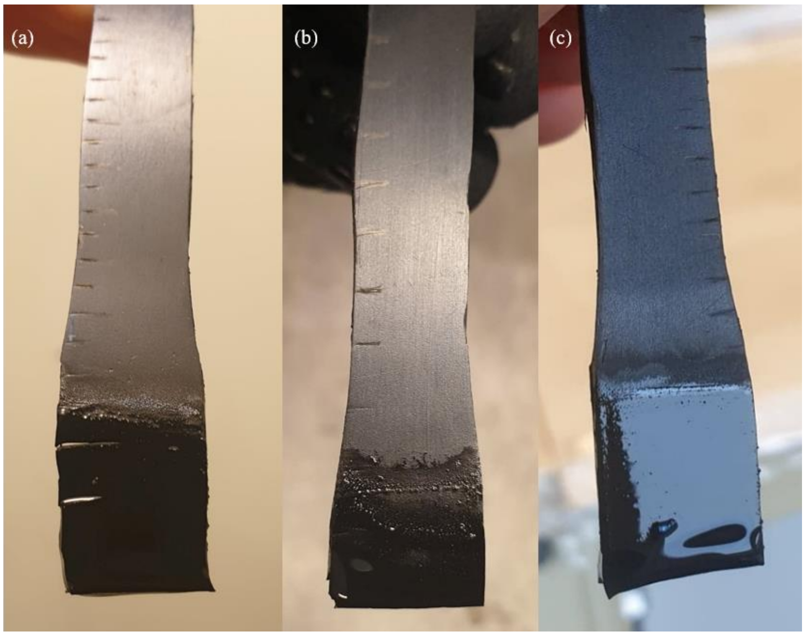


Figure 9. Three strands that have just been removed from the solvent. The strands in images (a) and (b) had vague zero-level (liquid level). The strand in image (c) had a distinguish zero level. Strand (a) and (c) are mark every 2.5 mm and (b) are marked every 5 mm.

Another problem was the fact that the diffusion up through the strands was slow, resulting in only one data point with a high error due to the diffuse zero level, see Figure 10. Hence, this setup gave no useful data for modelling since only two points were larger than zero. Additionally, the test with the rubber strands was time-consuming.

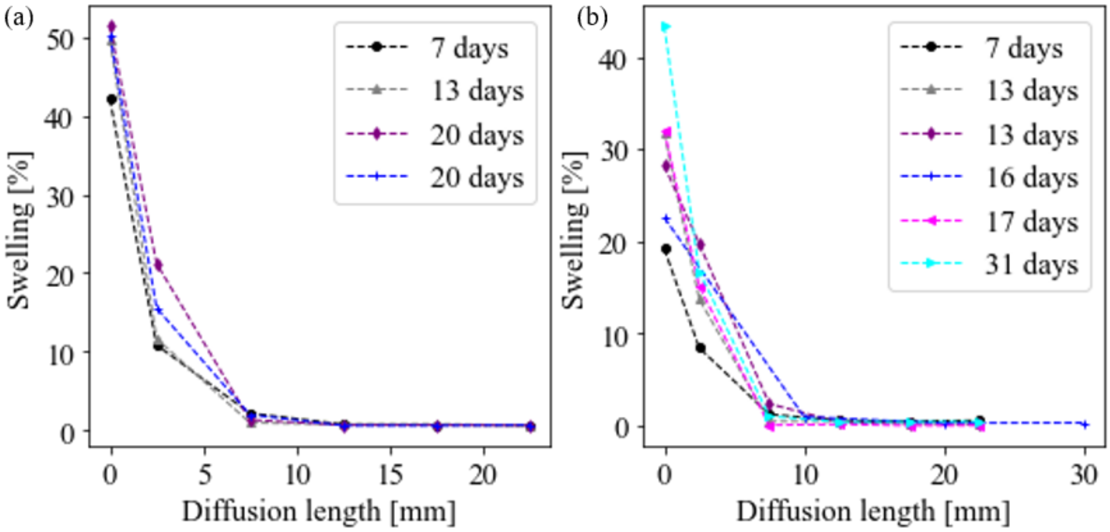


Figure 10. (a) EPDM-strand in oleic acid. (b) NBR-strand in triethyl citrate.

EPDM and pentadecane was the rubber-solvent combination that had the fastest rate of swelling compared to the others used in this project. Hence, the swelling distance was a bit longer compared to the other combinations, see Figure 11. However, the problem with the vague zero levels was still present.

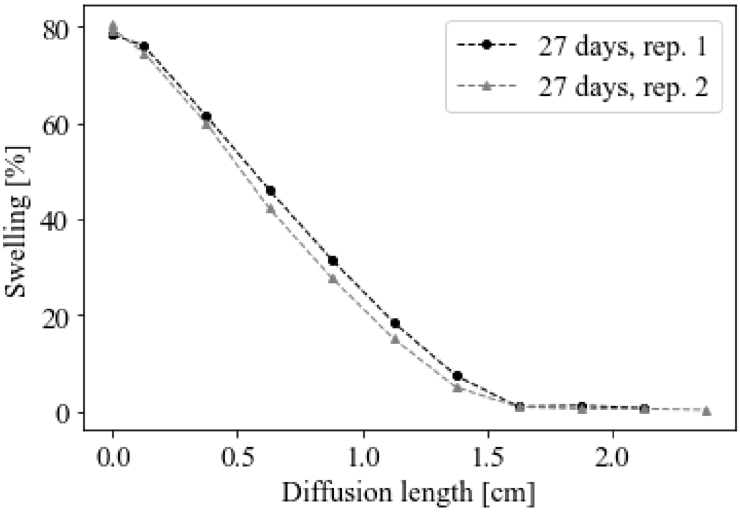


Figure 11. Swelling throughout the EPDM strands in pentadecane at 22 °C after 27 days. Rep. is short for replica. The experiment was conducted by placing one end of the rubber piece in pentadecane.

A remedy to increase the number of data points was to mark the stands every 2.5 mm instead of 5 mm. This gave more data points per test, which can be seen in Figure 11. Due to the vague zero level, an approximation was made for the error bars for the diffusive length. It was assumed to be ± 2.5 mm. This gave large error bars in the x-axis as seen in Figure 11.

According to the literature study (section 2.5), the rate of swelling increases with temperature, therefore, the strand setup was placed in an oven at 80 °C. One problem that occurred for the strands at 80 °C was the evaporation of the solvent. Consequently, the zero levels differed even more with time since the liquid level was adjusted in an attempt to keep the zero level constant. Also, at 80 °C the evaporation of the solvent could increase the uncertainty of observed swelling at short distances since rubber could also absorb vapour. Therefore, the observed swelling could be attributed by both vapour uptake and the solvent that diffused up through the rubber.

Even if the data gained from EPDM strands marked at each 2.5 mm (see Figure 11) was enough for modelling, the test was still time-consuming. Furthermore, the free swelling test had higher accuracy and was less time-consuming. Therefore, it would be advantageous to find a mathematical relationship between the free swelling tests and the diffusion distance. Even if this was outside of the scope, it was decided to further investigate this relationship.

4.1 Free swelling

4.1.1 Influence of geometry on diffusion

Figure 12 shows how the rate of swelling varies with the geometry of the test pieces. Small rubber pieces reach equilibrium faster than bigger pieces. Hence, the rate of swelling depends on the ratio between the volume and surface area.

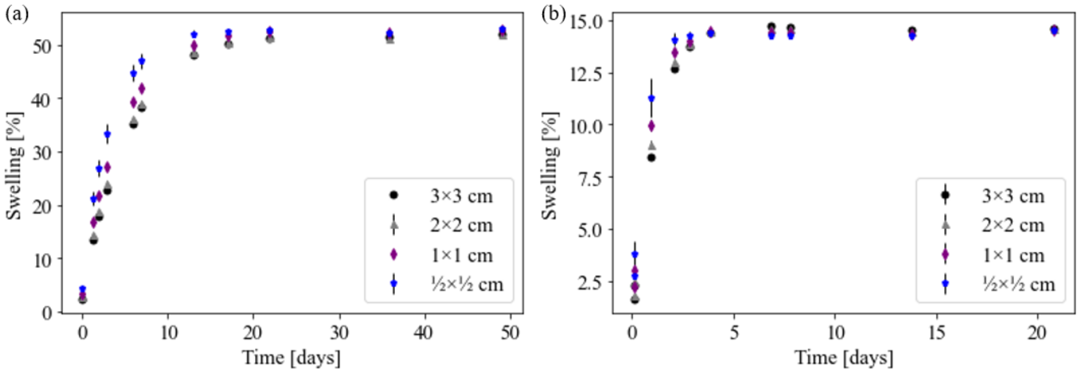


Figure 12. (a) EPDM and oleic acid 22 °C. (b) NBR and 1-octanol 50 °C

The fact that the ratio of surface to volume affected the rate of swelling could also be seen if observing the rubber pieces. In Figure 13 it is seen that the swelling is fastest at the sides since there is more surface area compared to the middle. The pieces had a flat surface before they were put into the solvent. Also, in Figure 13 it can be seen that the diffusion distance increases with swelling.

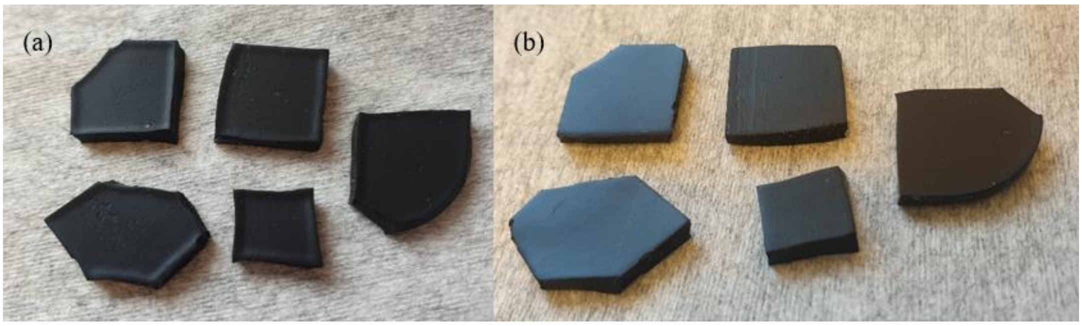


Figure 13. EPDM rubber piece. In (a) the pieces have been swelling for approx. 1 h in pentadecane at 40 °C. A clear volume increase is observed at the sides. (b) The same pieces after approx. 1 day of swelling. The whole pieces have an even volume increase.

Due to these results that were expected, the question occurs if the diffusion coefficient should be calculated with the characteristic length. As mentioned in section 2.8, the thickness of the swelling rubber is required to calculate the diffusion coefficient. [24], [26]–[28] It is unsure from the literature if it was assumed that the piece can be regarded as an infinitely large piece i.e., the characteristic length is equal to the thickness (the diffusion in an infinitely large piece is closest to one dimensional). Hence, both the characteristic length and the thickness were used to evaluate the diffusion coefficients.

4.1.2 Calculations of diffusion constants

Firstly, all combinations of rubber, solvents and temperature were fitted to equation (16) to determine if the diffusion could be approximated with Fickian. The obtained n and k values are given for EPDM in Table 2 and Table 3 for NBR, along with the R^2 values. The raw data used can be seen in appendix A.

Table 2. Calculated n-values, k-values, and goodness of fit, R^2 for EPDM in a selected set of solvents.

Temperature (°C)	n	k	R^2
Pentadecane			
22	0.61	1.42	0.95
40	0.60	1.93	0.98
50	0.48	1.77	0.94
80	0.49	2.73	0.96
Oleic acid			
22	0.50	0.28	0.98
50	0.51	0.61	0.99
80	0.54	1.25	0.97
1-Octanol			
22	0.45	0.35	0.98
50	0.47	0.82	0.99
80	0.50	1.71	0.99
1-Decanol			
22	0.44	0.27	0.99
50	0.45	0.64	0.99
80	0.43	1.37	0.96

Table 3. Calculated n-values, k-values, and goodness of fit, R^2 for NBR in a selected set of solvents.

Temperature (°C)	***n***	***k***	***R^2***
Triethyl citrate			
22	0.55	0.10	0.99
40	0.51	0.23	0.99
50	0.51	0.31	1.00
1-Octanol			
22	0.49	0.21	0.99
50	0.51	0.65	0.91
80	0.51	1.62	0.97
1-Decanol			
22	0.45	0.20	0.98
50	0.44	0.59	0.99
80	0.49	1.35	0.96

As can be seen in Table 2 and 3, the *n* coefficients are between 0.43-0.61 with a good fit above 0.9 for all combinations. This indicates that some combinations deviate slightly from Fickian diffusion (since they are not exactly 0.5). However, Fickian diffusion is a good assumption for the combinations investigated in this project since most of the *n*-values are close to 0.5 (average deviations from 0.5 were 8.2 % EPDM and 5.1 % for NBR). EPDM and pentadecane at 22 °C had the highest deviation of 22 %.

Afterwards, the data for free swelling were preprocessed and fitted accordingly to equation (14) in section 2.8. The diffusion coefficients were calculated from the slope, see equation (15) in section 2.8. Diffusion coefficient (*D)*, and goodness of fit (R^2) are given in Table 4 for EPDM and Table 5 for NBR. The raw data can be seen in appendix A. The calculated slopes and intercepts are presented in appendix B.

Table 4. Calculated diffusion coefficients, D, and goodness of fit, R^2, for EPDM and a selected set of solvents using the thickness of the sheet.

Temperature (°C)	D (m^2/s)	R^2
Pentadecane		
22	$1.66 \cdot 10^{-11}$	0.95
40	$2.96 \cdot 10^{-11}$	0.98
50	$2.78 \cdot 10^{-11}$	0.95
80	$6.35 \cdot 10^{-11}$	0.95
Oleic acid		
22	$6.77 \cdot 10^{-13}$	0.96
50	$3.23 \cdot 10^{-12}$	0.99
80	$1.42 \cdot 10^{-11}$	0.98
1-Octanol		
22	$7.39 \cdot 10^{-13}$	0.97
50	$5.31 \cdot 10^{-12}$	0.99
80	$2.58 \cdot 10^{-11}$	0.99
1-Decanol		
22	$4.18 \cdot 10^{-13}$	0.98
50	$2.74 \cdot 10^{-12}$	0.97
80	$1.82 \cdot 10^{-11}$	0.97

Table 5. The calculated diffusion coefficient, D, and goodness of fit, R^2, for NBR and a selected set of solvents using the thickness of the sheet.

Temperature (°C)	D (m^2/s)	R^2
Triethyl citrate		
22	$1.28 \cdot 10^{-13}$	0.97
40	$4.45 \cdot 10^{-13}$	0.95
50	$8.73 \cdot 10^{-13}$	0.99
1-Octanol		
22	$2.86 \cdot 10^{-13}$	0.97
50	$3.73 \cdot 10^{-12}$	0.95
80	$2.36 \cdot 10^{-11}$	0.97
1-Decanol		
22	$1.97 \cdot 10^{-13}$	0.94
50	$2.17 \cdot 10^{-12}$	0.97
80	$1.72 \cdot 10^{-11}$	0.95

As seen in Table 4 and 5, the goodness of fit was above 0.9 for all rubber and solvent combinations. The calculated diffusion coefficients seem reasonable since they are in the same order of magnitude as the diffusion coefficients in the literature study (section 2.8).

As discussed previously in section 4.1.1, the size influences the swelling rate. Hence, the diffusion coefficients were also determined with the characteristic length. For these calculations, it was assumed that the test pieces with a weight between 0.2 and 0.3 g had a quadratic geometry with the size of 10×10 mm^2. The characteristic length of these tests pieces was calculated to 1.4 mm (calculations shown in appendix C). Following the same procedure as above but replacing h_0 with the characteristic length in equation (14), resulted in the diffusion coefficients presented in Table 6 and 7 for EPDM and NBR respectively.

Table 6. Calculated diffusion coefficients, D, and goodness of fit, R^2 for EPDM and a selected set of solvents using the characteristic length.

Temperature (°C)	**D (m^2/s)**	**R^2**
	Pentadecane	
22	$7.68 \cdot 10^{-12}$	0.98
40	$1.49 \cdot 10^{-11}$	0.98
50	$1.64 \cdot 10^{-11}$	0.98
80	$3.24 \cdot 10^{-11}$	0.95
	Oleic acid	
22	$3.69 \cdot 10^{-13}$	0.99
50	$1.67 \cdot 10^{-12}$	0.99
80	$7.04 \cdot 10^{-12}$	0.98
	1-octanol	
22	$3.74 \cdot 10^{-13}$	0.99
50	$2.69 \cdot 10^{-12}$	0.99
80	$1.32 \cdot 10^{-11}$	0.99
	1-decanol	
22	$2.24 \cdot 10^{-13}$	0.99
50	$1.41 \cdot 10^{-12}$	0.97
80	$9.11 \cdot 10^{-12}$	0.97

Table 7. Calculated diffusion coefficients, D, and goodness of fit, R^2, for NBR and a selected set of solvents using the characteristic length.

Temperature (°C)	***D* (m²/s)**	***R*²**
Triethyl citrate		
22	$7.56 \cdot 10^{-14}$	0.97
40	$2.21 \cdot 10^{-13}$	0.95
50	$4.44 \cdot 10^{-13}$	0.99
1-octanol		
22	$1.44 \cdot 10^{-13}$	0.97
50	$2.00 \cdot 10^{-12}$	0.95
80	$7.56 \cdot 10^{-11}$	0.97
1-decanol		
22	$1.16 \cdot 10^{-13}$	0.94
50	$1.36 \cdot 10^{-12}$	0.97
80	$8.24 \cdot 10^{-12}$	0.95

When comparing the diffusion coefficients calculated with the thickness (Table 4 and 5) and the characteristic length (Table 6 and 7); the diffusion coefficients calculated with the characteristic length are smaller. This was not unexpected since the characteristic length is shorter than the thickness.

It can be discussed whether utilizing equation (14) is appropriate to use for the combinations in this study. As mentioned previously (section 2.8) equation (14) is valid at initial times. At 40, 50 and 80 °C for all combinations and EPDM in pentadecane at 22 °C, 4-6 data points were taken under the first day. For the other combinations at 22 °C, data points were taken each day (besides from weekends) during the first 1-2 weeks and then more sporadically until equilibrium was reached. At 22 °C equilibrium was reached after 2-3 months for some combinations. 1-2 weeks can be seen as initial relative to 2-3 months. Moreover, for the calculations of the slope, only values that were below 90 % of equilibrium level was used to ensure that only initial times were used.

Furthermore, it was investigated if there was a linear relationship between the diffusion coefficient calculated from the characteristic length as a function of the temperature and the solvent parameters. The diffusion coefficients determined from the characteristic length were used since these values are more suitable for gaskets as they have varying size and geometry, that cannot be approximated with a large plane sheet. A multiple linear regression was performed and the data was preprocessed by taking the logarithm of the diffusion coefficients which generated equation (16) for EPDM with a fit of 0.95. The Hansen’s solubility parameters of the solvents have been assumed to be temperature independent in the investigated temperature interval since the thermal expansion factors were not found for all solvents. It was out of scope to determine expansion factors for this project. The values given in Table 1 (section 2.7) was assumed to be valid at 25 °C. The temperature was not stated in Table A1 in [21].

$$lnD_{EPDM} = 0.050T + 0.19\delta_d - 1.32\delta_p + 0.29\delta_h - 0.0099V_m \qquad (17)$$

V_{m} is the molar volume of the solvent. For NBR the goodness of fit was 0.99 and resulted in equation (18).

$$lnD_{NBR} = 0.074T - 0.0026\delta_d - 0.0032\delta_p - 0.024\delta_h - 0.012V_m \qquad (18)$$

In Figure 14, the experimental diffusion coefficients are plotted versus the predicted values using equation (17) and (18) for EPDM and NBR respectively. If the predicted value would be equal to the experimental, all data points in Figure 14 would have been on the straight black line. Hence, the predictions of equation (17) and (18) deviates slightly from the measured values.

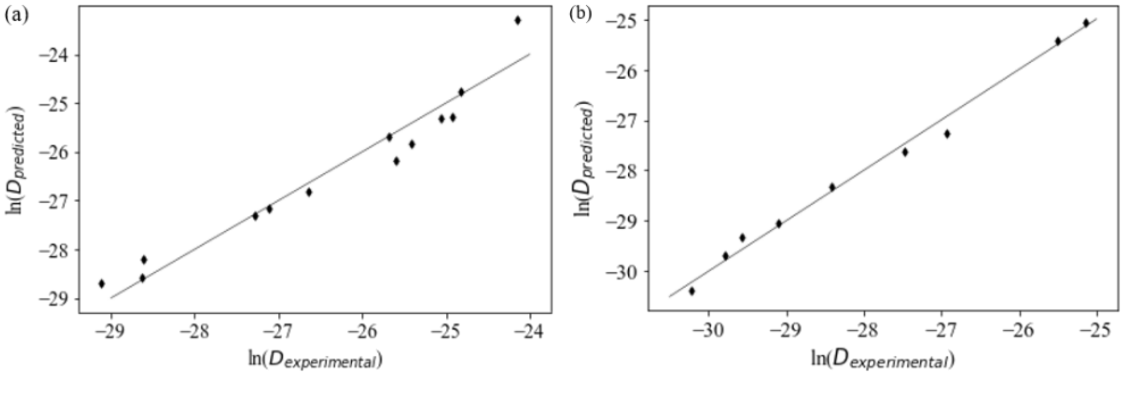


Figure 14. (a) Diffusion coefficients for EPDM predicted with equation (17) plotted versus experimental values. The black line is y = x. (b) Diffusion coefficients for NBR predicted with equation (18) plotted versus experimental values. The black line is equal to y = x.

4.1.3 Equilibrium level

Figure 15 showcases the equilibrium swelling level versus temperature for all rubber and solvent combinations. A linear trend can be observed for all combinations, see Figure 15.

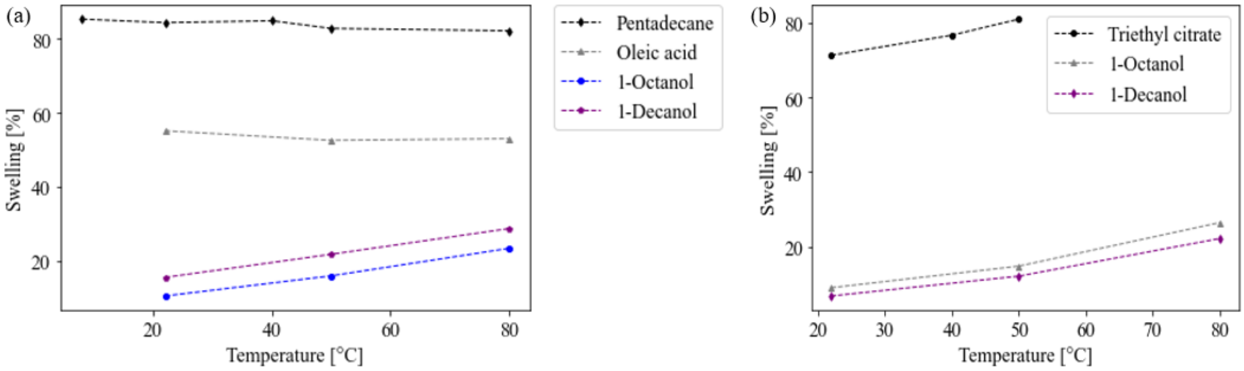


Figure 15. The swelling equilibrium plotted versus temperature for (a) EPDM and (b) NBR for different solvents.

It was observed that the equilibrium increased with temperature besides from EPDM swelled in pentadecane and oleic acid which appeared to be temperature independent. This temperature independence was not expected. The intermolecular forces between EPDM and pentadecane and oleic acid are mainly dispersion forces. Dispersive forces are less sensitive to temperature compared to hydrogen bonding and might be the reason for the temperature independence. [21] Moreover, the elastic modulus of rubber increases with increasing temperature. An increase in elastic modulus means that the rubber stiffens and the swelling decreases. Perhaps the increase of swelling because of the temperature increasing (energy of mixing increases) is as large as the decrease in swelling caused by the increasing elastic modulus of the rubber. This might be due to the dispersion forces have a relative low temperature sensitivity.

To be noted, the equilibrium level for EPDM in pentadecane at 80 °C, varied between 74 and 80 %. It could also be seen that the swelling equilibrium for EPDM in pentadecane had a decrease with increasing temperature. A decreasing equilibrium level with increasing temperature has been discussed by Wang et. al., and they suggested that it can be due to the desorption rate of additives in rubber also increases with increasing temperatures [29]. Perhaps, the equilibrium swelling level is temperature independent for EPDM in pentadecane, but the desorption rate of additives increases with the temperature. Therefore, the equilibrium swelling level appears to be lower for EPDM in pentadecane at 80 °C. However, this explanation might not be likely for the EPDM rubber used in this report, as this particular quality does not include many additives that could desorb.

Further, a linear relationship could be found for the equilibrium swelling level as a function of the solvent parameters and the temperature. This resulted in equations (19) and (20) with R^2 of 0.98 and 1.00 respectively for EPDM and NBR.

$$Q_{eq,EPDM} = 0.015T + 1.51\,\delta_d - 9.91\,\delta_p - 0.20\,\delta_h + 0.075\,V_m \tag{19}$$

$$Q_{eq,NBR} = 0.31T + 1.47\,\delta_d + 1.90\delta_p + 14.21\,\delta_h + 0.71\,V_m \tag{20}$$

Equations (19) and (20) were determined with temperatures between 22 and 80 °C. Therefore, caution should be taken when extrapolating the equations to either higher or lower temperatures. For example, equation (19) might give a negative Q if the temperature is zero and the used solvent has a, e.g., high polar forces.

In Figure 16, the experimental swelling equilibria are plotted versus the predicted values using equation (19) and (20) for EPDM and NBR respectively.

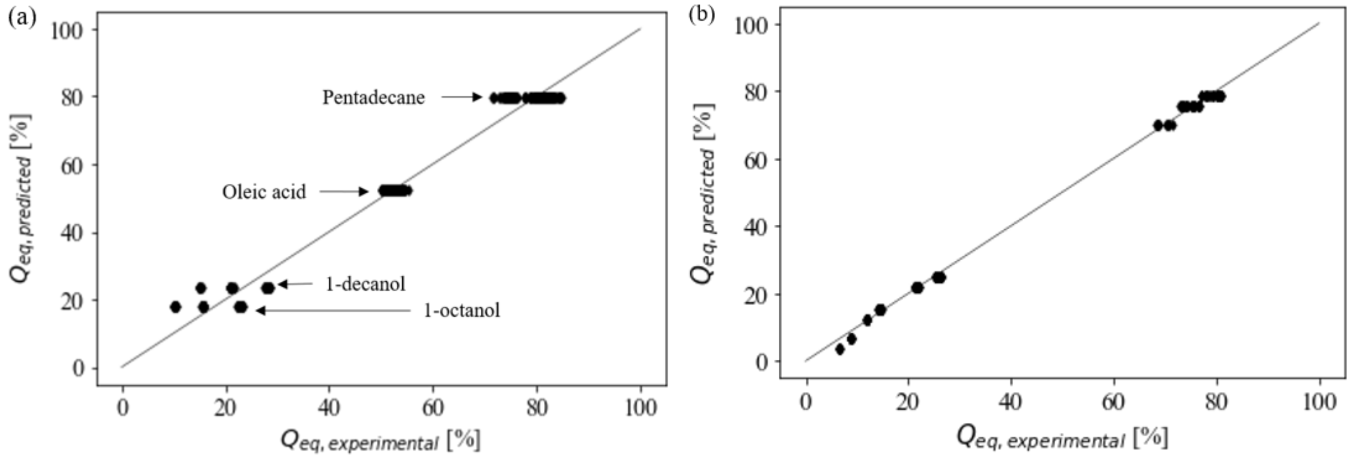


Figure 16. (a) Equilibrium swelling level for EPDM predicted with equation (19) plotted versus experimental values. The black line is y = x. The black arrows point to which solvents the horizontal spread of data points comes from (b) Equilibrium swelling level for NBR predicted with equation (20) plotted versus experimental values. The black line is y = x.

As can be seen in Figure 16, there is a horizontal spread around the black line, especially for (a). This spread represents the variation in equilibrium level. The equilibrium level varies from test piece to test piece, in particular EPDM and pentadecane, as discussed previously in this section. The spread of 1-octanol and 1-decanol are more likely to be because of the model not being able to predict the temperature dependence. That's why there are three distinct clusters of data points in a horizontal line, each cluster representing a different temperature. The model for EPDM might be less good to predict the temperature dependence since two of the solvents used (pentadecane and oleic acid) does not have a temperature dependence. It is seen in Figure 16(b) that the model for NBR do predict the temperature dependence better since there is less spread of the data point in the horizontal line compared to EPDM.

Because equations (17), (18), (19) and (20) are only based on three and four solvents respectively for NBR and EPDM; there is an uncertainty if these models would reliably predict the diffusion coefficients and the swelling equilibrium for solvents with a vastly different chemical structure than the solvents investigated in this project.

It could be possible to make a general equation for all type of rubbers and solvents, but this would require a test setup with more than two different rubbers. With only two rubbers it is not possible to find constants representing all rubbers.

4.2 Rubber strands

Predictive models were obtained by using equation (12) in section 2.8 and the calculated diffusion coefficients for EDPM in pentadecane at 22 °C and 80 °C from Table 4 and 6. It was assumed that the end of the rubber in contact with the solvent immediately reached equilibrium at the surface, i.e., C_1 was assumed to be the equilibrium level at free swelling. Further, C_0 was zero since there was no solvent present in the rubber strand from the beginning. The first two strand sets investigated had been submerged into the solvent for 27 days at 22 °C and 7 days for 80 °C, the result is shown in Figure 17 and 18.

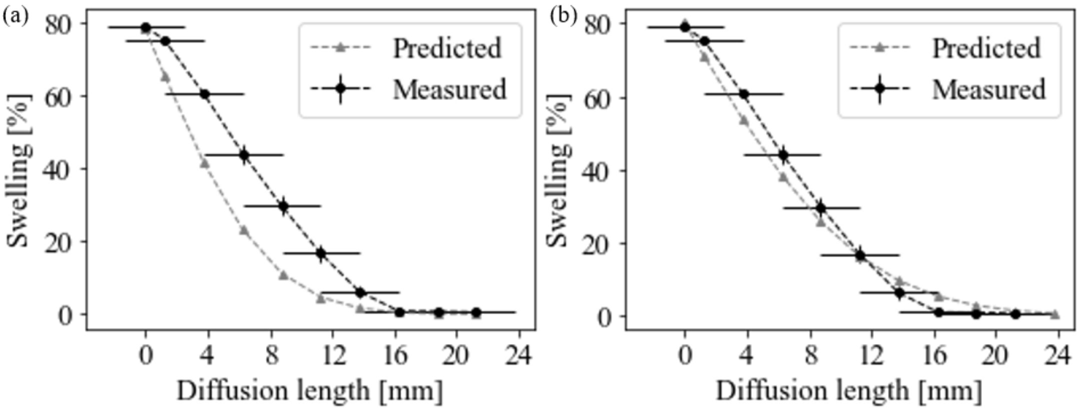


Figure 17. Swelling of EPDM in pentadecane at 22 °C as a function of diffusion length. Both measured (black)lines are EPDM-strands in pentadecane after 27 days. (a) The predicted line was calculated with the diffusion constant determined from the characteristic length. (b) The predicted line was calculated with the diffusion constant determined from the thickness.

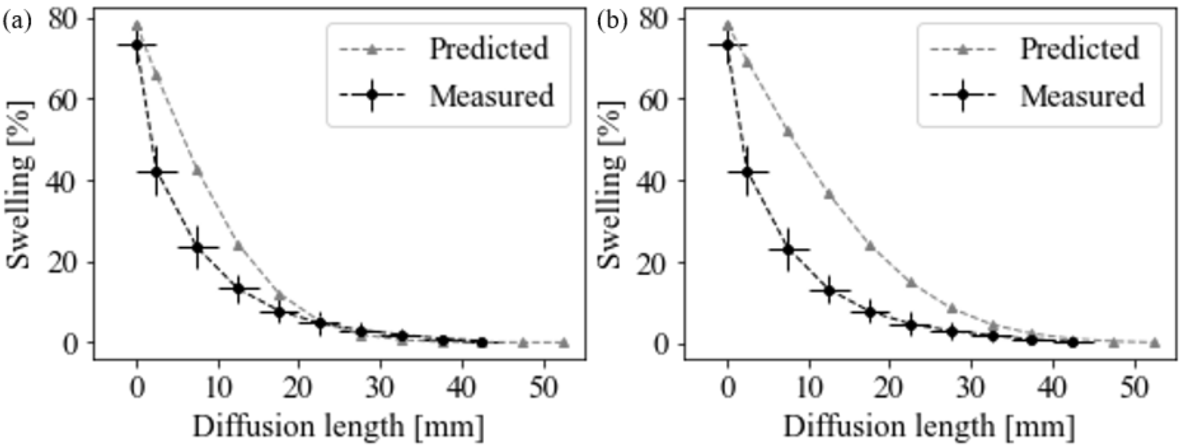


Figure 18. Swelling of EPDM in pentadecane as a function of diffusion length. Both measured (black) lines are EPDM-strands in pentadecane at 80 °C after 7 days. (a) The predicted line was calculated with the diffusion constant determined from characteristic length. (b) The predicted line was calculated with the diffusion constant determined from the thickness.

As seen in Figure 17, the model using the diffusion coefficient determined from the thickness of the test pieces gave a better prediction compared to the diffusion coefficient determined from characteristic length for the strands at room temperature. The other way around was seen for the strands at 80 °C, see Figure 18. This result is contradicting. The strands at 80 °C had larger error bars compared to the strands at room temperature. One reason for this can be that the liquid level differed more for the strands at 80 °C. Another thing to note is that the error bars in the y-axis for the room temperature are calculated from two datasets, so they have lower reliability compared to the strands at 80 °C that are calculated from three datasets (see appendix A, Fig. A9).

Furthermore, the additional times, 13 and 16 days were investigated for EPDM-strands in pentadecane at 22 °C. As can be seen in Figure 19 and 20, the model using the diffusion coefficient determined with the characteristic length predicts the values from 13 and 16 days better than the model including the diffusion coefficient calculated with the thickness. The diffusion coefficients calculated with characteristic length predicted the diffusion distance closer in three out of four cases.

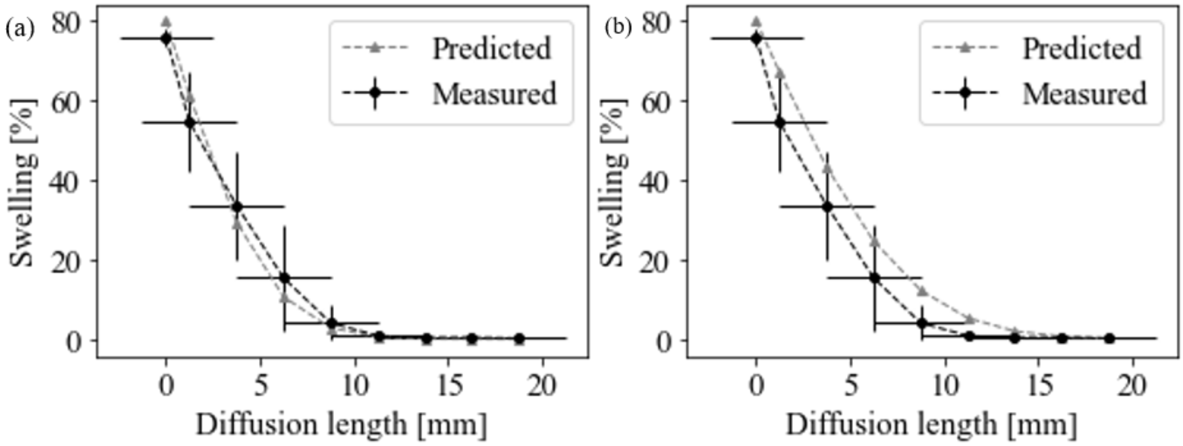


Figure 19. Swelling of EPDM in pentadecane as a function of diffusion length. Both measured (black) lines are EPDM-strands in pentadecane at room temperature after 13 days. (a) The predicted line was calculated with the diffusion constant determined from characteristic length. (b) The predicted line was calculated with the diffusion constant determined from the thickness.

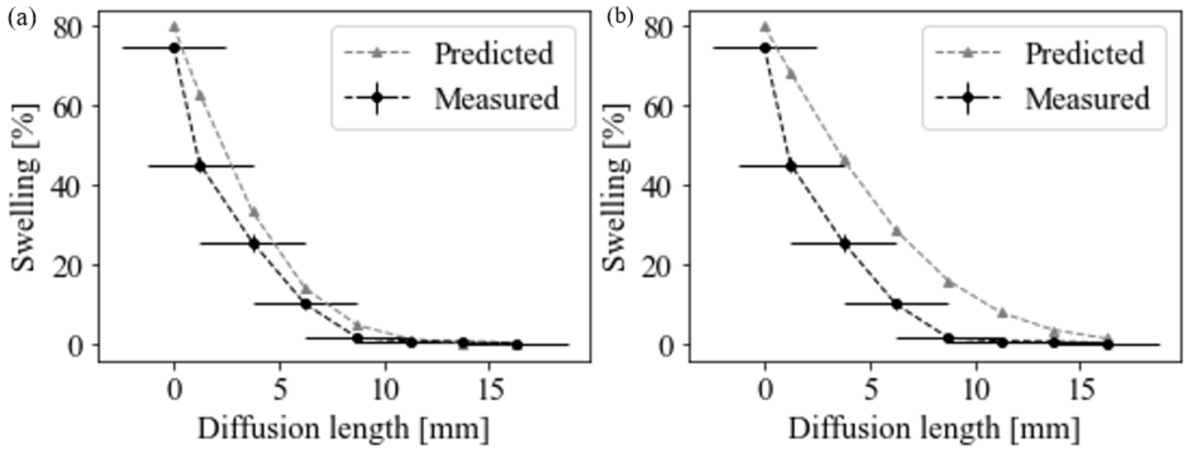


Figure 20. Swelling of EPDM in pentadecane as a function of diffusion length. Both measured (black) lines are EPDM-strands in pentadecane at room temperature after 16 days. (a) The predicted line was calculated with the diffusion constant determined from characteristic length. (b) The predicted line was calculated with the diffusion constant determined from the thickness.

In Figure 19, the errors along the y-axis for 13 days are large. The errors were calculated with only two values (as for 16 days). The big errors can be explained with the vague zero levels as discussed in section 4.1.1; in this case, the vague zero levels resulted in wrongly positioned swelling values.

When investigating the diffusion length of fluid in rubber, it was seen that nothing diffused higher than 15 mm at 22 °C and approx. 30 mm in 80 °C. One thought was that it might be due to the gravity, even if this is not so likely since the diffusion in rubbers also are slow for free swelling tests at room temperature where the gravity is negligible. A solution for the slow diffusion could be to find solvents that swells rubber faster. However, some fast-swelling solvents, such as toluene, are volatile even at room temperature. A possible solution to minimize the evaporation of the solvent can be by using a lid.

The rubber strands might be a problem of three dimensions, the solvent diffuse in the z-y-x-axis i.e., up, and throughout the cross-section. Three-dimensional problems usually lead to complicated mathematical expressions. Therefore, it was assumed that the solvent in the rubber strand could only diffuse in one direction (upwards), i.e., making the three-dimensional problem into a one-dimensional problem. The rubber strands were assumed to be a one-dimensional problem since the length of the strands was much larger than the cross-section i.e., the diffusion through the cross-section is negligible compared to the diffusion upwards. One way to further strengthen the assumption is to cut strands with a smaller width e.g., instead of 10 mm cut 5 mm. Decreasing the thickness might be complicated since the standard thickness of rubber sheets delivered to Alfa Laval is 2 mm.

4.3 Other results of interest

4.3.1 NBR in triethyl citrate at 80 °C

NBR in triethyl citrate at 80 °C did not reach equilibrium, see Figure 21. The NBR continued to swell for 26 days. On day 26 the test was terminated since the lab equipment was needed for other tests and the desired level would not be reached. Two suggestions for this unexpected result were that the solvent changed with time (e.g., degradation due to high temperatures) or that the crosslink density changed over time due to unknown chemical reactions (chemical relaxation).

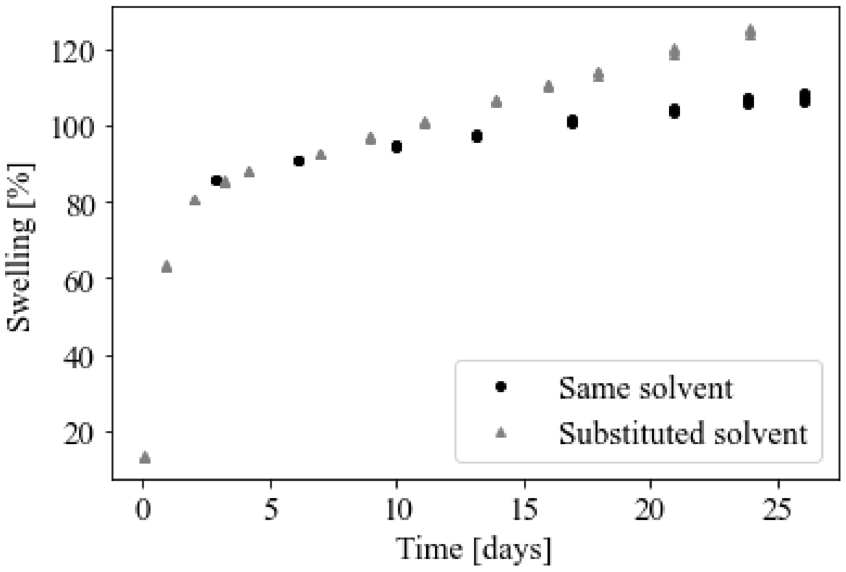


Figure 21. Time dependence of swelling NBR in triethyl citrate at 80 °C. The grey triangles are the data points from the test where the solvent was substituted every other day. The black circles are the data points from the test where the same solvent was used throughout the test.

Since one thought was that the unexpected result was due to degradation of triethyl citrate at 80 °C, two different tests were performed. In the first test, the triethyl citrate was substituted with a fresh batch every other day at 80 °C. However, this also led to a similar behaviour as when not replacing the triethyl citrate, see Figure 21. In the second test, the old triethyl citrate that had been at 80 °C for over 35 days was compared to the new triethyl citrate in the free swelling test at room temperature. As can be seen in Figure 22, the new and reused triethyl citrate behaved almost identically.

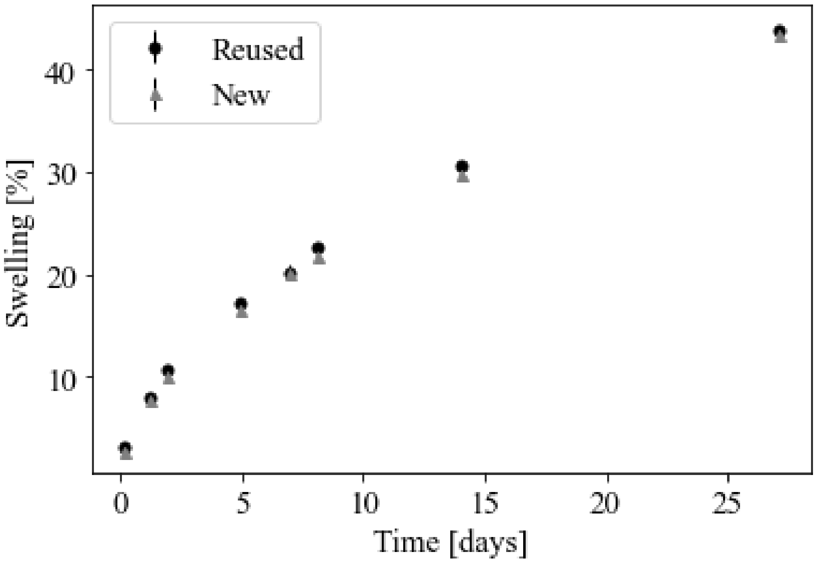


Figure 22. Swelling NBR in triethyl citrate at room temperature as a function of time. Triethyl citrate that had been used at 80 °C for approx. 25 days was reused in a swelling test of NBR to see if it behaved in the same way as the new triethyl citrate. The grey triangles are the data from the new triethyl citrate, and the black circles are the data from the reused triethyl citrate.

Consequently, the unexpected result that was seen for NBR in triethyl citrate at 80 °C did not depend on degradation of the solvent. It is most likely that the result was due to chemical relaxation, but this was not investigated further since it was outside of the scope of this project. As a consequence, the combination of NBR and triethyl citrate was further only investigated at temperatures 50 °C and below. The chemical relaxation is sensitive to temperature; hence, lower temperatures should be more suitable for the test, which was the observed case, see appendix A, Figure A1.

4.3.2 Oleic acid ageing test

The oleic acid used had a purity of 85 %. Therefore, an ageing test was done to ensure that the composition of the oleic acid did not impact the swelling equilibrium. As seen in Figure 23, there was no significant difference between the reused oleic acid and new. Hence, it can be assumed that the remaining 15 % of compounds had a similar structure and swelling effect as oleic acid.

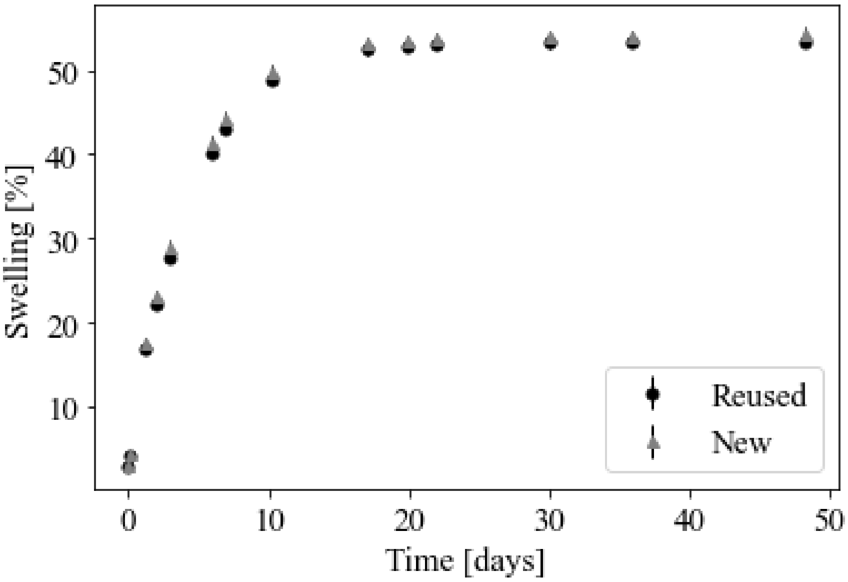


Figure 23. Swelling EPDM in Oleic acid as a function of time at room temperature. Oleic acid that already had been used for a swelling test was reused to another to see if it behaved the same way as new oleic acid. The grey triangles are the data from the new oleic acid and the black circles are the data from the reused oleic acid.

4.3.3 The effect of compression on swelling

The rubbers that were subjected to a compressive force had an applied deformation of approx. 25 %. The result from the pressure test is shown in Figure 24. The data from the reopened and closed setup gave unexpected results. Hence, it was difficult to evaluate if they reached equilibrium or not. Even if the results were vague, it seemed like the rubbers had not reached equilibrium at the end of the test. The other two unopened tests were terminated since the project reached its end. This means that the other two unopened setups probably did not reach the desired equilibrium level.

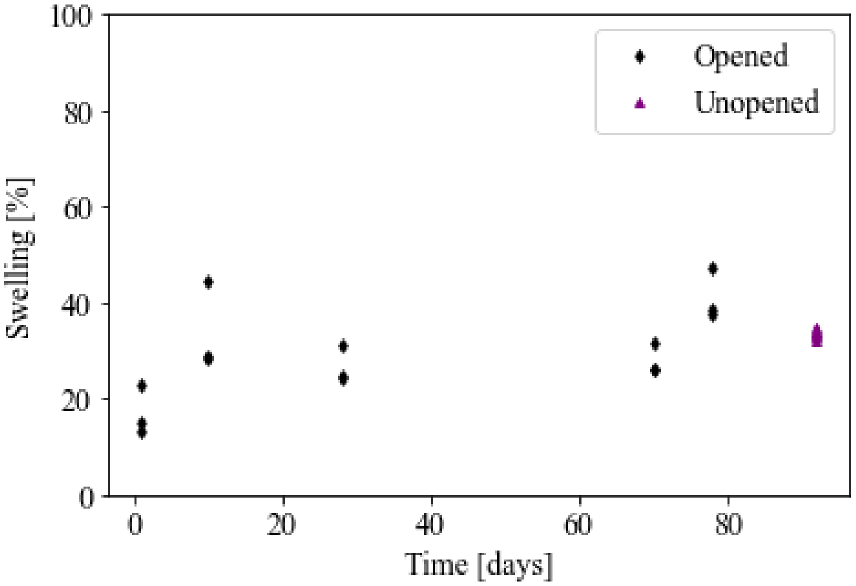


Figure 24. Time dependence of swelling for EPDM compressed between two metal plates in pentadecane. The black markers correspond to the rubber pieces from the set-up that was opened. The purple markers correspond to those pieces that were in the set-ups that were unopened.

The unopened setups seemed to have reached a reliable value since all six pieces gave approximately the same swelling level. The mean value of the six pieces was 34 % after 91 days. By comparison, the equilibrium value was approx. 80 % for swelling without compression and was already reached after approx. 1 day. This indicates that our calculated models overestimate the swelling level for gaskets in heat exchangers since gaskets are subjected to significant compression. Perhaps, the swelling decreases under compression as the elastic modulus also increases. As discussed previously, a increase in the elastic modulus, stiffens the rubber and the swelling decreases. The reason for a potential decrease in swelling rate can be explained by the rubber not being fully in contact with the solvent which means that the solvent has fewer ways to enter the rubber.

The large spread of data from the rubber pieces from the reopened and closed setup might depend on the replacement of the rubber pieces. The rubbers may have been replaced in different ways resulting for example, in more contact with the solvent or higher pressure. It can also be some effect of the coming and going pressure but in that case, all three pieces would have changed the same way, which they did not do.

4.4 General discussion

The presented empirical models (equations (19) and (20)) are most likely not to be fully applicable for gasket materials used in a heat exchanger since gaskets are under compression. The compression forces in the heat exchanger would probably decrease the swelling, which means that swelling equilibria obtained by free swelling are an overestimation for the gaskets.

The gasket in the heat exchanger is bigger than the test pieces used in this project. As mentioned previously, the size affects the rate of swelling. The diffusion coefficients determined with characteristic length should be independent of the size. Therefore, the models calculating the diffusion coefficients (equation (17) and (18)) should also be suitable for diffusion in gaskets without pressure. However, the diffusion coefficients might not be usable for gaskets compressed in heat exchangers; since it has not been investigated in this study how the compression affects the diffusion.

Factors that may affect the measuring of the swelling are if there are any solvent or water from the washing step left at the surface of the rubber. Other factors that are less likely are incorrect reading of the scale. The scale itself only has an error of 0.0001 g. The contribution to the error from the scale should be negligible compared to the other errors mentioned previously, such as the diffuse zero level on the rubber strands, and left-over solvent or water on the rubber pieces when weighing.

4.5 Methodology

In this section, a short stepwise summary of the method used in this project is given, i.e., determine diffusion coefficients and length. This can be used as a guide if it is desirable to perform similar experiments.

1. Cut 10×10 mm^2 test pieces from a 2 mm thick sheet, approx. weight of 0.2 to 0.3 g. (These pieces will have a characteristic length of 1.4 mm)
2. Cover the pieces completely in the selected solvent and place them at the desired temperature. Make sure there is enough solvent to keep the pieces completely covered even after swelling.
3. Take 4-5 data points to see the time dependence. (The more points taken, the higher reliability of the results, but a minimum of 4-5 points should be taken to perform a linear regression.) Depending on the temperature and the compatibility between the

rubber and the solvent, the 4-5 data points might need to be taken on the same day or over a longer period.

4. A data point after 1 week should give or be close to the equilibrium level at least for temperatures of 50 °C and above. Generally, at 22 °C, the swelling rate is much slower and can take up to 2-3 months before equilibrium is reached.
5. Preprocess and evaluate the data accordingly to equation (14) utilizing the characteristic length instead of thickness.
6. Calculate the diffusion coefficient from the slope, equation (15).
7. Plugin the diffusion coefficient into equation (12) to approximate the diffusion distance.

5 Conclusion

In this report, the time-dependence of swelling in two rubber materials, EPDM and NBR, was investigated with 4 and 3 solvents respectively. Also, the diffusion distance, i.e., the swelling at certain positions in rubber strands, was investigated with the same two rubbers, EPDM and NBR, with 2 respectively 1 solvent. Diffusion coefficients were calculated for all combinations of rubber and solvent. Further, a stepwise guide describing the method in this report was presented.

To conclude the results, a compressive pressure on the rubber had an evident effect on the swelling but was difficult to quantify. Furthermore, the swelling rate was affected by the size; smaller pieces swell faster than big ones. One unexpected result was that the diffusion up through rubber strands was slow. The diffusion was too slow to collect usable data for all our combinations within the time limit of this project. However, it seems promising to predict diffusion length with calculated diffusion coefficients. The diffusion coefficient determined from the characteristic length gave, in most cases, the best prediction of the diffusion length.

Finally, it was seen that Fickian diffusion was a good enough assumption for the rubber and solvent combinations tried in this study. Since Fickian diffusion could be assumed, a diffusion coefficient could be calculated for all combinations, both by using the thickness of the sheet and characteristic length.

It seems promising to quantify swelling equilibria and diffusion coefficients with temperature and solvent parameters for gasket materials. The models ((equations [17], [18], [19] and [20])) for quantification are most likely not applicable for gaskets in a heat exchanger, but for the gasket material, the models are valid and have high goodness of fit.

6 Future work

It would have been desirable to test the models (equations [17], [18], [19] and [20]) for temperature and solvent which the models are not based on, but this was not possible within our time limit. It would also be interesting to find models that could predict swelling and diffusivity for a mixture of solvents since most fluids in heat exchangers are a mixture of liquids. Furthermore, it would also have been of interest to investigate how the temperature dependence of the solubility parameter affects swelling rate and equilibrium. This could be done by constructing models using solvents with known expansion factors.

If more time had been available, we would also have wanted to test more combinations for the rubber strands at higher temperatures. To improve the setup at higher temperatures, an evaluation of how to place a lid to both minimize the vapour uptake and the evaporation of solvent should also be done. A suggestion of placement to minimize the vapour uptake is to only cover the submerged part of the rubber strand. Moreover, a possibility to replace the rubber strand test might be to instead slice test pieces from a free swelling test and measure the concentration of the solvent as a function of the diffusion distance with e.g., thermogravimetric analysis (assuming that the solvent evaporates at lower temperatures than the degradation of the polymer).

Some further work could be done to find a model that is suitable for all rubber and solvent combinations; therefore, more combinations should be evaluated and try to find a function that works for all combinations. It is not likely that a general model is possible since each rubber recipe has different solubility parameters (e.g., one EPDM rubber does not have to be identical to another if they are produced by different companies).

It would also be interesting to estimate the time it takes for the solvent to diffuse into the centre of the test pieces theoretically from the calculated diffusion coefficients and then compare them to the experimental times from the free swelling tests. This comparison would also indicate whether the calculated diffusion coefficients are reasonable. Further, the diffusion coefficients could be calculated by including more terms in equation (13). These diffusion coefficients can be compared to the diffusion coefficients determined from equation (14) that only include the intial term. This would indicate if the inital term is enough to get a good approximation or if more terms needed.

Further investigate how compression affect swelling would be of interest, for example, to see how other combinations behave. If using the same type of setup that was used in this project (see Figure 6), a suggestion is to use more setups; because then it is possible to eliminate the reopening and closing of the setup which would be desirable since it gave results that were difficult to interpret.

Lastly, in a heat exchanger, the gaskets are placed in channels which leads to a complex rubber-solvent contact. This rubber-solvent contact was not taken into consideration in the setup used for compression. Conducting the experiments in situ with a heat exchanger or an arrangement similar to a heat exchanger would have been optimal. In that sense, how the complex rubber-solvent contact surface, how the temperature difference and how the overall complexity impacts the swelling, will be achieved. The data obtained from this setup could also be used to validate simpler models.

References

[1] “Alfa Laval.” https://www.alfalaval.com/ (accessed May 13, 2021).

[2] B. E. (Bruce E. Johansen, “Encyclopedia of American Indian Contributions to the World: 15,000 Years of Inventions and Innovations (review),” *Am. Indian Q.*, vol. 26, no. 4, pp. 667–673, 2002, doi: 10.1353/aiq.2004.0007.

[3] *Gummiteknologi, en introduktion*. Accessed: May 02, 2021. [Online]. Available: https://laroverket.com/en-introduktion/

[4] L. R. G. Treloar, *The physics of rubber elasticity*, 3. ed. Clarendon P., 1975. Accessed: May 02, 2021. [Online]. Available: http://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=cat07147a&AN=lub.1872840&site=eds-live&scope=site

[5] G. R. Hamed, “Materials and Compounds,” in *Engineering with Rubber*, A. N. Gent, Ed. Hanser, 2012, pp. 11–36. doi: 10.3139/9783446428713.002.

[6] A. Stevenson and R. Campion, “Durability,” in *Engineering with Rubber*, 3rd ed., München: Carl Hanser Verlag GmbH & Co. KG, 2012, pp. 205–257. doi: 10.3139/9783446428713.007.

[7] “EPDM.” http://polymerdatabase.com/Elastomers/EPDM.html (accessed May 11, 2021).

[8] “NBR.” http://polymerdatabase.com/Elastomers/NBR.html (accessed May 11, 2021).

[9] J. Hasa and M. Ilavský, “Deformational, swelling, and potentiometric behavior of ionized poly(methacrylic acid) gels. II. Experimental results,” *J. Polym. Sci. Polym. Phys. Ed.*, vol. 13, no. 2, pp. 263–274, Feb. 1975, doi: 10.1002/pol.1975.180130204.

[10] M. Akhtar, S. Qamar, and T. Pervez, *Swelling Elastomer Applications in Oil and Gas Industry*. 2012.

[11] O. Farid, “Investigating membrane selectivity based on polymer swelling,” Ph.D., University of Nottingham, 2011. Accessed: May 14, 2021. [Online]. Available: http://eprints.nottingham.ac.uk/11774/

[12] P. J. Flory, *Principles of polymer chemistry*. Cornell University Press, 1953. Accessed: May 19, 2021. [Online]. Available: http://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=cat07147a&AN=lub.1378417&site=eds-live&scope=site

[13] M. Zielińska, R. Seyger, W. K. Dierkes, D. Bielinski, and J. W. M. Noordermeer, “Swelling of EPDM rubbers for oil-well applications as influenced by medium composition and temperature. Part I. Literature and theoretical background,” *Elastomery*, vol. T. 20, nr 2, 2016, Accessed: May 14, 2021. [Online]. Available: http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.baztech-14da0222-966e-41bb-8e7a-4e6e842cd7a4

[14] S. H. Botros and A. M. E. Sayed, “Swelling behavior of NR/EPDM rubber blends under compression strain,” *J. Appl. Polym. Sci.*, vol. 82, no. 12, pp. 3052–3057, 2001, doi: https://doi.org/10.1002/app.2160.

[15] F. Neff, A. Lion, and M. Johlitz, “Modelling diffusion induced swelling behaviour of natural rubber in an organic liquid,” *ZAMM - J. Appl. Math. Mech. Z. Für Angew. Math. Mech.*, vol. 99, no. 3, p. e201700280, 2019, doi: https://doi.org/10.1002/zamm.201700280.

[16] M. S. Hedenqvist and U. W. Gedde, “Parameters affecting the determination of transport kinetics data in highly swelling polymers above Tg,” *Polymer*, vol. 40, no. 9, pp. 2381–2393, Apr. 1999, doi: 10.1016/S0032-3861(98)00453-4.

[17] G.-R. Shan, P.-Y. Xu, Z.-X. Weng, and Z.-M. Huang, “Oil-absorption function of physical crosslinking in the high-oil-absorption resins,” *J. Appl. Polym. Sci.*, vol. 90, no. 14, pp. 3945–3950, 2003, doi: https://doi.org/10.1002/app.12971.

[18] D. Messmer, O. Bertran, R. Kissner, C. Alemán, and A. D. Schlüter, “Main-chain scission of individual macromolecules induced by solvent swelling.,” *Chem. Sci.*, vol. 10, no. 24, pp. 6125–6139, Jun. 2019, doi: 10.1039/c9sc01639b.

[19] J. R. Fried, *Polymer science and technology*, Third Edition. Prentice Hall, 2014. Accessed: May 03, 2021. [Online]. Available: http://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=cat07147a&AN=lub.4546854&site=eds-live&scope=site

[20] D. W. van Krevelen, *Properties of Polymers*. Elsevier, 2012.

[21] C. M. Hansen, *Hansen Solubility Parameters: A User’s Handbook, Second Edition*. CRC Press, 2007.

[22] PubChem, “Pentadecane.” https://pubchem.ncbi.nlm.nih.gov/compound/12391 (accessed May 03, 2021).

[23] K. A. Dill and S. Bromberg, *Molecular driving forces : statistical thermodynamics in biology, chemistry, physics, and nanoscience*, 2. ed. Garland Science, 2011. Accessed: May 06, 2021. [Online]. Available: http://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=cat07147a&AN=lub.1994591&site=eds-live&scope=site

[24] J. Crank and E. P. J. Crank, *The Mathematics of Diffusion*. Clarendon Press, 1979.

[25] N. G. Lehtinen, “1 Error function erf x and complementary er- ror function erfc x,” p. 10.

[26] “Structural characteristics and swelling mechanism of two commercial nitrile-butadiene elastomers in various fluids,” *Polym. Test.*, vol. 31, no. 4, pp. 564–571, Jun. 2012, doi: 10.1016/j.polymertesting.2012.02.007.

[27] S. George, K. T. Varughese, and S. Thomas, “Molecular transport of aromatic solvents in isotactic polypropylene/acrylonitrile-co-butadiene rubber blends,” *Polymer*, vol. 41, no. 2, pp. 579–594, Jan. 2000, doi: 10.1016/S0032-3861(99)00208-6.

[28] W. E. Rudzinski, S. F. Harlapur, and T. M. Aminabhavi, “Evaluation of solvent resistivity of fluoropolymers for use as backup membranes in isocyanate samplers,” *J. Appl. Polym. Sci.*, vol. 62, no. 10, pp. 1587–1595, 1996, doi: https://doi.org/10.1002/(SICI)1097-4628(19961205)62:10<1587::AID-APP10>3.0.CO;2-#.

[29] H. Wang, X. Liu, P. Apostolidis, S. Erkens, and T. Scarpas, “Numerical investigation of rubber swelling in bitumen,” *Constr. Build. Mater.*, vol. 214, pp. 506–515, Jul. 2019, doi: 10.1016/j.conbuildmat.2019.04.144.

[30] C. Kumnuantip and N. Sombatsompop, “Dynamic mechanical properties and swelling behaviour of NR/reclaimed rubber blends,” *Mater. Lett.*, vol. 57, no. 21, pp. 3167–3174, Jul. 2003, doi: 10.1016/S0167-577X(03)00019-3.

Appendix A

Includes the raw data from the free swelling and rubber strands experiments.

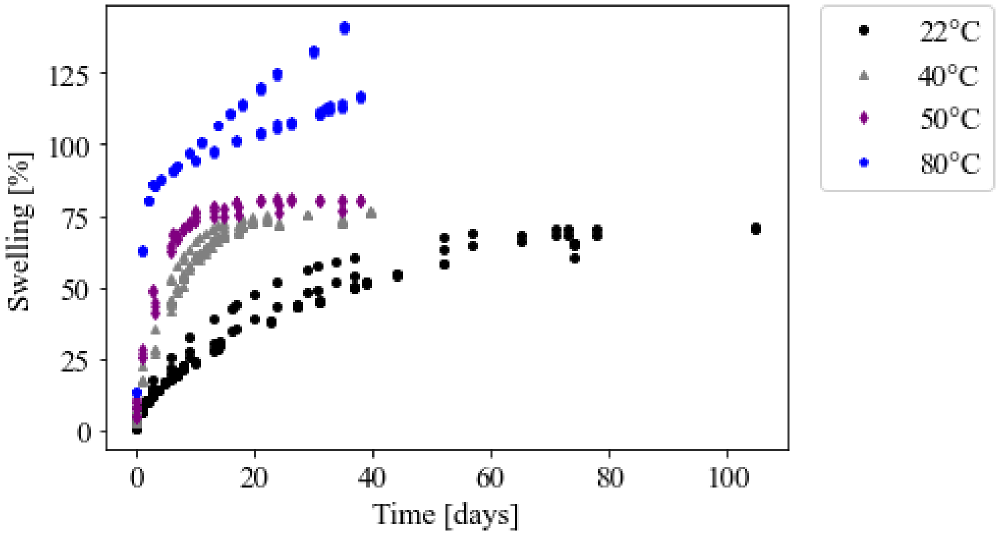


Figure A1. Free swelling of NBR in triethyl citrate at 22, 40, 50, and 80 °C. The experiment was conducted by completely submerging NBR pieces in triethyl citrate.

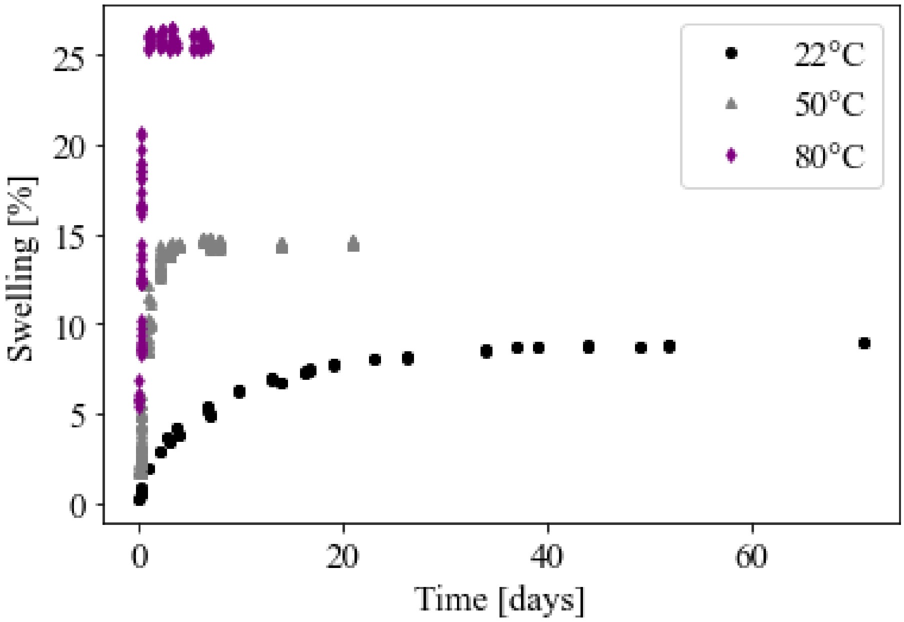


Figure A2. Free swelling of NBR in 1-octanol 22, 50, and 80 °C. The experiment was conducted by completely submerging NBR pieces in 1-octanol.

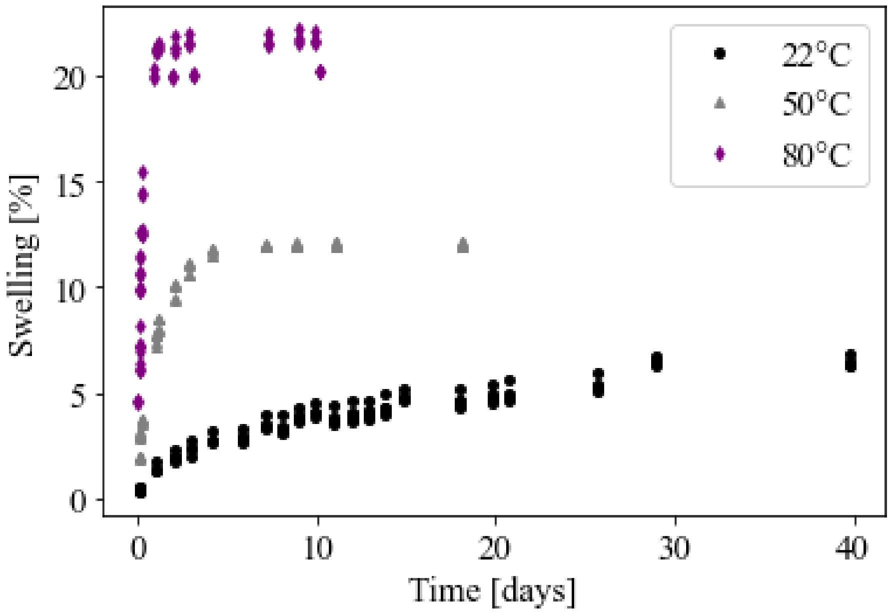


Figure A3. Free swelling of NBR in 1-decanol 22, 50, and 80 °C. The experiment was conducted by completely submerging NBR pieces in 1-decanol.

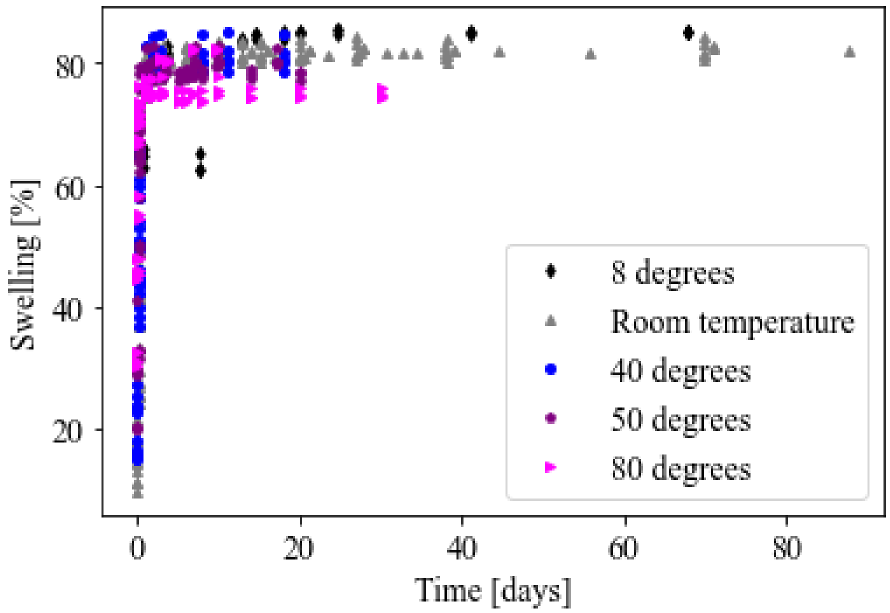


Figure A4. Free swelling of EPDM in pentadecane 22, 40, 50, and 80 °C. The experiment was conducted by completely submerging EPDM pieces in pentadecane.

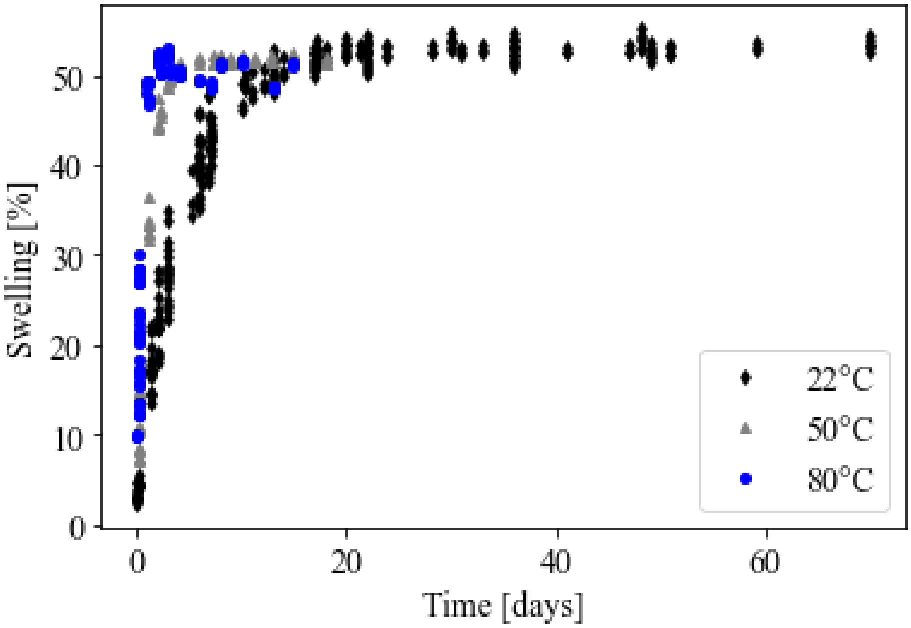


Figure A5. Free swelling of EPDM in oleic acid at 22, 50, and 80 °C. The experiment was conducted by completely submerging EPDM pieces in oleic acid.

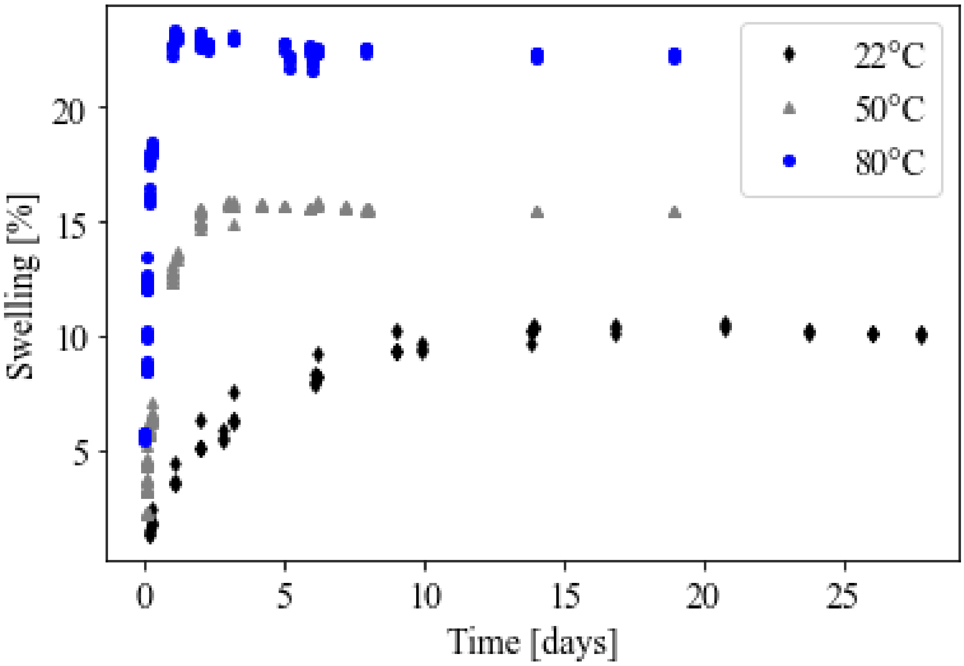


Figure A6. Free swelling of EPDM in 1-octanol 22, 50, and 80 °C. The experiment was conducted by completely submerging EPDM pieces in 1-octanol.

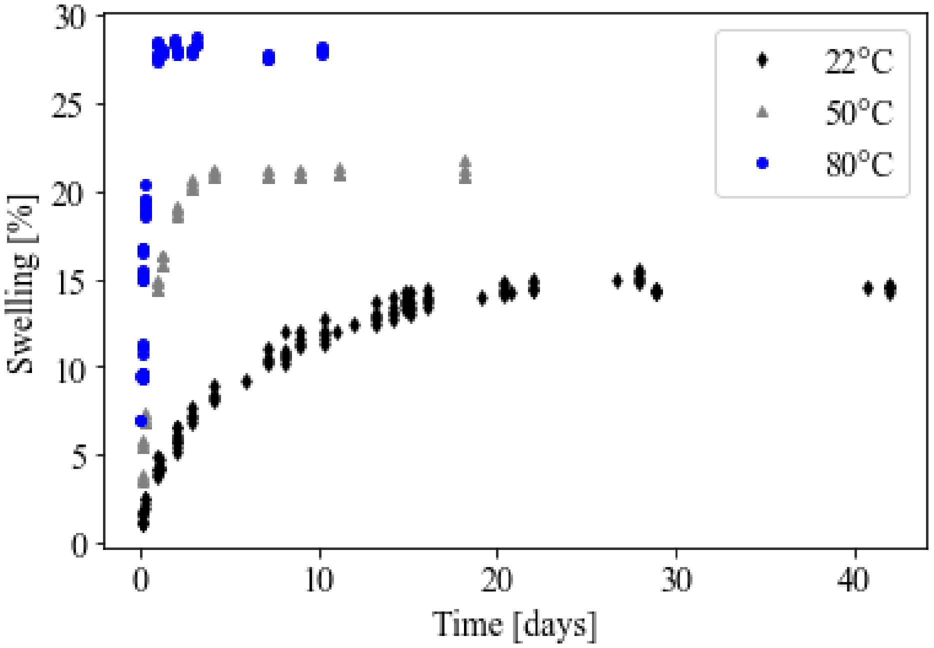


Figure A7. Free swelling of EPDM in 1-decanol 22, 50, and 80 °C. The experiment was conducted by completely submerging EPDM pieces in 1-decanol.

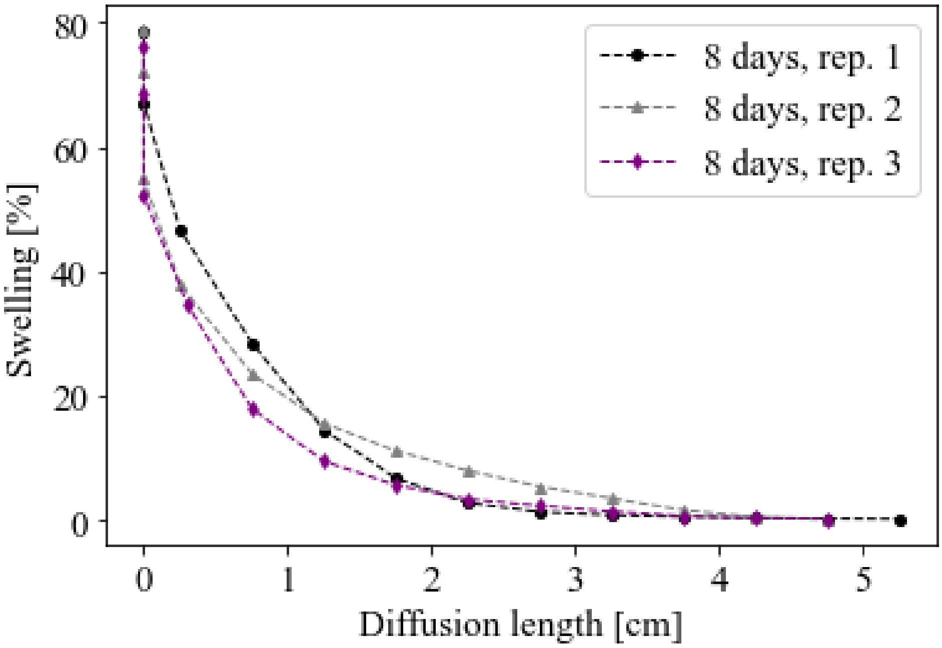


Figure A8. Swelling throughout the EPDM strands in pentadecane at 80 °C after 8 days Rep. is short for replica. The experiment was conducted by placing one end of the rubber piece in pentadecane.

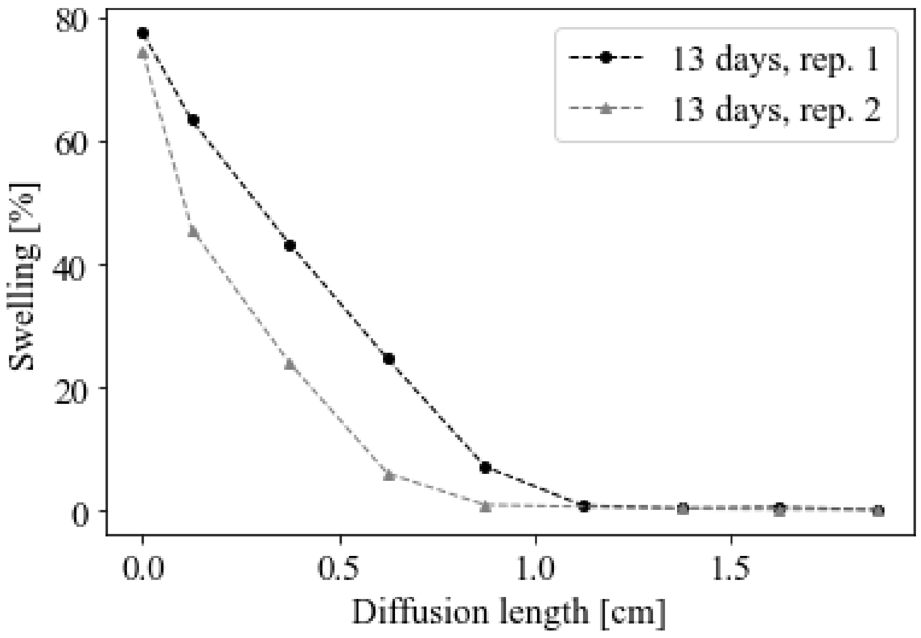


Figure A9. Swelling throughout the EPDM strands in pentadecane at 22 °C after 13 days. Rep. is short for replica. The experiment was conducted by placing one end of the rubber piece in pentadecane.

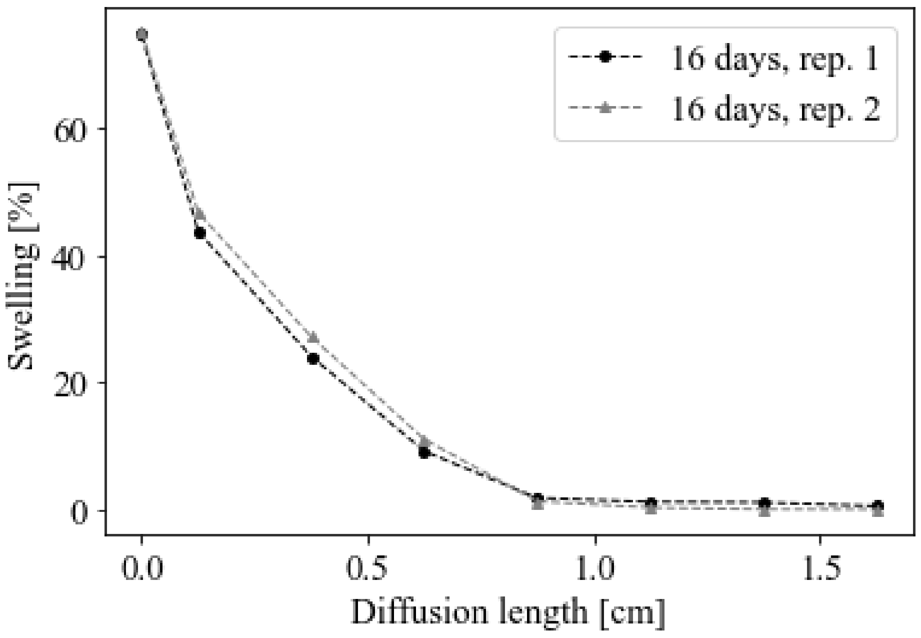


Figure A10. Swelling throughout the EPDM strands in pentadecane at 22 °C after 16 days. Rep. is short for replica. The experiment was conducted by placing one end of the rubber piece in pentadecane.

Appendix B.

Extension of Table 4, 5, 6 and 7 including the calculated slopes and intercepts. from the calculations of the diffusion coefficient using equation (14).

Table B1. Calculated diffusion coefficients, D, intercepts, slopes, and goodness of fit, R^2, for EPDM and a selected set of solvents using the thickness of the sheet.

Temperature (°C)	***D*** **(m^2/s)**	**Intercept**	**Slope**	**R^2**
Pentadecane				
22	$1.66 \cdot 10^{-11}$	-0.067	$9.19 \cdot 10^{-6}$	0.95
40	$2.96 \cdot 10^{-11}$	-0.077	$1.23 \cdot 10^{-5}$	0.98
50	$2.78 \cdot 10^{-11}$	0.032	$1.19 \cdot 10^{-5}$	0.95
80	$6.35 \cdot 10^{-11}$	0.045	$1.8 \cdot 10^{-5}$	0.95
Oleic acid				
22	$6.77 \cdot 10^{-13}$	0.022	$1.86 \cdot 10^{-6}$	0.96
50	$3.23 \cdot 10^{-12}$	0.011	$4.06 \cdot 10^{-6}$	0.99
80	$1.42 \cdot 10^{-11}$	-0.035	$8.5 \cdot 10^{-6}$	0.98
1-Octanol				
22	$7.39 \cdot 10^{-13}$	0.067	$1.94 \cdot 10^{-6}$	0.97
50	$5.31 \cdot 10^{-12}$	0.037	$5.2 \cdot 10^{-6}$	0.99
80	$2.58 \cdot 10^{-11}$	0.011	$1.15 \cdot 10^{-5}$	0.99
1-Decanol				
22	$4.18 \cdot 10^{-13}$	0.064	$1.46 \cdot 10^{-6}$	0.98
50	$2.74 \cdot 10^{-12}$	0.075	$3.73 \cdot 10^{-6}$	0.97
80	$1.82 \cdot 10^{-11}$	0.054	$9.63 \cdot 10^{-6}$	0.97

Table B2. Calculated diffusion coefficients, D, intercepts, slopes, and goodness of fit, R^2, for NBR and a selected set of solvents using the thickness of the sheet.

Temperature (°C)	*D* (m^2/s)	Intercept	Slope	R^2
Triethyl citrate				
22	$1.28\cdot10^{-13}$	-0.009	$8.54\cdot10^{-7}$	0.97
40	$4.45\cdot10^{-13}$	0.045	$1.55\cdot10^{-6}$	0.95
50	$8.73\cdot10^{-13}$	0.008	$2.12\ \cdot10^{-6}$	0.99
1-Octanol				
22	$2.86\cdot10^{-13}$	0.061	$1.28\cdot10^{-6}$	0.97
50	$3.73\cdot10^{-12}$	0.011	$4.36\cdot10^{-6}$	0.95
80	$2.36\cdot10^{-11}$	-0.004	$1.11\cdot10^{-5}$	0.97
1-Decanol				
22	$1.97\cdot10^{-13}$	0.077	$1.00\cdot10^{-6}$	0.94
50	$2.17\cdot10^{-12}$	0.088	$3.33\cdot10^{-6}$	0.97
80	$1.72\cdot10^{-11}$	0.008	$9.35\cdot10^{-6}$	0.95

Table B3. Calculated diffusion coefficients, D, intercepts, slopes, and goodness of fit, R^2, for EPDM and a selected set of solvents using the characteristic length.

Temperature (°C)	*D* (m^2/s)	Intercept	Slope	R^2
Pentadecane				
22	$7.68\cdot10^{-12}$	-0.058	$6.25\cdot10^{-6}$	0.98
40	$1.49\cdot10^{-11}$	-0.083	$8.71\cdot10^{-6}$	0.98
50	$1.64\cdot10^{-11}$	-0.0098	$9.15\cdot10^{-6}$	0.98
80	$3.24\cdot10^{-11}$	0.045	$1.29\cdot10^{-5}$	0.95
Oleic acid				
22	$3.69\cdot10^{-13}$	0.011	$1.37\cdot10^{-6}$	0.99
50	$1.67\cdot10^{-12}$	-0.0012	$2.92\cdot10^{-6}$	0.99
80	$7.04\cdot10^{-12}$	-0.032	$5.99\cdot10^{-6}$	0.98
1-Octanol				
22	$3.74\cdot10^{-13}$	0.051	$1.38\cdot10^{-6}$	0.99
50	$2.69\cdot10^{-12}$	0.034	$3.70\cdot10^{-6}$	0.99
80	$1.32\cdot10^{-11}$	0.0091	$8.19\cdot10^{-6}$	0.99
1-Decanol				
22	$2.24\cdot10^{-13}$	0.05632038	$1.07\cdot10^{-6}$	0.99
50	$1.41\cdot10^{-12}$	0.06965638	$2.68\cdot10^{-6}$	0.97
80	$9.11\cdot10^{-12}$	0.05546227	$6.81\cdot10^{-6}$	0.97

Table B4. Calculated diffusion coefficients D, intercepts, slopes, and goodness of fit, R^2, for NBR and a selected set of solvents using the characteristic length.

Temperature (°C)	***D*** **(m^2/s)**	**Intercept**	**Slope**	**R^2**
Triethyl citrate				
22	$7.56 \cdot 10^{-14}$	-0.020	$6.19 \cdot 10^{-7}$	0.97
40	$2.21 \cdot 10^{-13}$	0.028	$1.08 \cdot 10^{-6}$	0.95
50	$4.44 \cdot 10^{-13}$	0.0018	$1.52 \cdot 10^{-6}$	0.99
1-Octanol				
22	$1.44 \cdot 10^{-13}$	0.050	$8.57 \cdot 10^{-7}$	0.97
50	$2.00 \cdot 10^{-12}$	0.017	$3.19 \cdot 10^{-6}$	0.95
80	$7.56 \cdot 10^{-11}$	-0.014	$7.84 \cdot 10^{-6}$	0.97
1-Decanol				
22	$1.16 \cdot 10^{-13}$	0.057	$7.71 \cdot 10^{-7}$	0.94
50	$1.36 \cdot 10^{-12}$	0.080	$2.45 \cdot 10^{-6}$	0.97
80	$8.24 \cdot 10^{-12}$	0.0098	$6.51 \cdot 10^{-6}$	0.95

Appendix C

Includes the calculations of the characteristic length for a sheet with the geometry of 10×10×2 mm^3.

Firstly, the characteristic length, *l*, is defined in equation (C1).

$$l = \frac{V}{A_{surface}} \tag{C1}$$

Where V is the volume and A_{surface} is the surface area. For a sheet sample, equation (C1) can be written as in equation (C2).

$$l = \frac{h \cdot W \cdot b}{2(h \cdot b + h \cdot W + W \cdot b)} \tag{C2}$$

W is the width, and b is the length of the sheet. Inserting the dimensions 10×10×2 mm^3, l can be numerical calculated as in equation (C3).

$$l = \frac{2 \cdot 10 \cdot 10\ mm^3}{2(2 \cdot 10\ mm^2 + 2 \cdot 10\ mm^2 + 1 \cdot 1\ mm^2)} \approx 0.7\ mm \tag{C3}$$

The characteristic length determined in C3 corresponds to half of the thickness. This can be seen when calculating the characteristic length for a thin infinitely large piece according to equation (C2) is $l = h/2$. For the calculations in this report, it is desired to define the characteristic length so it corresponds to the whole thickness. Hence, the characteristic length was determined to 1.4 mm.