



TAMPERE UNIVERSITY OF TECHNOLOGY

SUSANNA MIETTINEN

OIL INDUCED SWELLING IN THERMOELASTIC MATERIALS

Master of Science Thesis

Examiner : Professor Pentti Järvelä
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Työn tarkoituksena oli löytää uusi RoHS direktiivin mukainen tiivistemateriaali ABB Oy:n valmistamiin taajuusmuuttajiin. Materiaalin tulee solveltua käytettäväksi kohteissa, joissa se saattaa altistua kemikaaleille ja öljylle. Materiaalin etsinnän lisäksi, työn tarkoitus oli kartoittaa syitä siihen, miksi materiaali turpoaa öljyissä. Työssä keskityttiin rakenteellisiin seikkoihin, sekä turpoavan kappaleen geometrian vaikutukseen.

Työn alussa, tiivistemateriaalille asetettiin joitakin rajoituksia. Uuden tiivistemateriaalin tuli olla RoHS direktiivin mukainen ja sen kovuuden tuli olla alle 60 Shore A asteikolla. Repimislujouden arvo tuli olla yli 23 kN/m ja materiaalilla piti olla jonkin tason paloluokitus. Tärkeimpänä kriteerinä oli kuitenkin materiaalin öljyjen kesto. Tiivistemateriaali ei saanut turvota öljyyn upotustestissä enempää kuin 25 tilavuusprosenttia.

Työn kirjallisuusosa esittelee neljä materiaaliryhmää, joiden ominaisuudet sopivat parhaiten etsittävään materiaaliin. Materiaaliryhmät ovat termoplastiset polyuretaanit, styreeni-eteenibuteeni-styreeni, termoplastiset vulkanisaatit sekä co-polyesteri pohjaiset elastomeerit. Näiden ryhmien tämän työn kannalta oleelliset ominaisuudet on esitelty omassa luvussaan. Kirjallisuusosuuksessa esitellään myös työssä testattavat materiaalit. Materiaalien valinta on tulosta materiaalien toimittajien ja tämän työn yhteistyötahona toimineen Trelleborg Industrial Products Finland Oy:n pitempiaikaisesta yhteistyöstä. Testattavia materiaaleja oli kuusi kappaletta. Kirjallisuusosuus käsittelee lisäksi myös elastomeerien turpoamiseen liittyviä rakenteellisia tekijöitä, joita ovat esimerkiksi rakenteen polaarisuus ja liukoisuuskerroin.

Työn kokeellinen osuus käsittelee upotuskokeita. Upotuskokeet tehtiin UL 157 standardin mukaisesti. Testikappaleet punnittiin aluksi ilmassa ja vedessä, jonka jälkeen ne upotettiin IRM 903 testiöljyyn 70 tunniksi. Upotuksen jälkeen kappaleet punnittiin jälleen vedessä ja ilmassa. Näiden massojen avulla saatiin laskettua testikappaleiden tilavuuden muutokset. Upotuskokeet tehtiin kolmessa vaiheessa. Ensimmäisessä vaiheessa testikappaleet olivat sauvan muotoisia ja niitä testattiin kahdella eri paksuudella. Toisessa vaiheessa testikappaleet olivat neliön muotoisia ja niitä testattiin kolmella eri paksuudella. Kolmannen vaiheen kappaleet olivat oikeiden käytössä olevien tiivisteiden muotoisia. Kaikki testikappaleet valmisti ja toimitti Trelleborg Industrial Products Finland Oy. Kokeellisessa osuudessa mitattiin myös testimateriaalien tiheydet.

Uputuskokeista saadun informaation ja materiaalin ominaisuuksien perusteella pystyttiin määrittämään parhaiten tähän käyttökohteeseen soveltuva materiaali. Kokeiden tulosten perusteella pyrittiin myös määrittämään kappaleen tilavuuden, pinta-alan, tilavuus/pinta-ala suhteen ja tiheyden vaikutus turpoamiseen. Määrittäminen tapahtui piirtämällä kuvaajat jokaisen tekijän suhteesta turpoamiseen ja etsimällä kuvaajista säännönmukaisuuksia. Ainoa tekijä, joka tutkimuksen mukaan vaikuttaa kappaleen turpoamiseen oli kappaleen tilavuus/pinta-ala suhde. Näytteiden turpoamisen aiheuttama tilavuuden muutos laitettiin samaan kuvaajaan näytteiden tilavuus/pinta-ala suhteiden kanssa ja näille pisteille saatiin hyvin paikkansa pitävä lineaarinen sovite.

Tässä työssä tehdyt testit jatkuvat, sillä työn edetessä löydettiin uusia kiinnostavia materiaaleja sekä kappalegeometrioita, eikä niitä ehditty testata tämän työn puitteissa.

ABSTRACT

TAMPERE UNIVERSITY OF TECHNOLOGY

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Major subject: Plastic Technology/Polymer Materials

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The purpose of this thesis was to find a new gasket material to be used in frequency converters manufactured by ABB. The new material has to comply to RoHS directive, because this material is going to replace the currently used material, which is not RoHS compliant. The material is going to be used in conditions, where it may be subjected to chemicals and especially oils, so it should have a good resistance to both. In addition to finding the material, this thesis considers factors affecting elastomer's swelling in oil.

Some requirements were set for the gasket material. The hardness of the material should not be over 60 Shore A and its tear strength should not be less than 23 kN/m. The material should also have a fire classification minimum of V1. The most important criterion was the oil resistance. Gasket material should not swell more than 25 percent from its initial volume when immersed in oil.

The literature part of this thesis consists of introducing four material groups which have such properties which are required from the gasket material and considers those properties. These four groups are thermoplastic polyurethanes, styrene-ethylene-butylene-styrene, thermoplastic vulcanizate elastomers and co-polyester based elastomers. The literature part also discusses the factors which help estimate the amount of swelling based on the structure of the thermoplastic elastomer.

The experiment part of this thesis introduces immersion tests which have been used to determine oil resistance of the test materials. Six materials were tested, the names of the materials are confidential, they are coded to be Materials A, B, C, D, E and F. From these results, the best suited material for the new gasket material was elected. Also from the results, it was possible to determine dependence of swelling on volume, area, volume/area ratio and density of the sample.

One suitable material was found in addition to a few others that require more testing. The only geometrical factor found to contribute materials swelling was volume/area ratio. Once the graph is made for a certain material, it helps to predict the swelling of a sample with a certain volume/area ratio made from the same material.

The tests made for this thesis will continue after this thesis is completed. Some new sample geometries and new materials will be tested.

FOREWORD

This Master of Science Thesis was co-operation with ABB Oy and Trelleborg Industrial Products Finland Oy. The aim of this thesis was to find a thermoplastic elastomer which fulfills the chemical resistance criteria set by Underwriters Laboratories. After a suitable material is found, it will be used to make gaskets to frequency transformers manufactured by ABB.

This thesis was made in Tampere University of Technology during 2009 and 2010. I would like to thank my supervisor Professor Pentti Järvelä and my instructor Vesa Palojoki for helping me with this thesis, as well as Pekka Uskali, Kari Nieminen and Elina Eklund for answering patiently to my questions.

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TERMS AND THEIR DEFINITIONS

A	Area
g/cm ³	Unit for density, kg/m ³
ρ	Greek alphabet rho for density
δ	Greek alphabet sigma for solubility parameter
mm	Measure of length, 10 ⁻³ m
M ₁	Weight of the specimen on air before the test
M ₂	Weight of the specimen in water before the test
M ₃	Weight of the specimen on air after the test
M ₄	Weight of the specimen in water after the test
MPa	Measure of pressure, 10 ⁶ Pa
V	Volume
ΔV	Difference of final volume and initial volume
V/A ratio	Ratio of volume and area
Shore A	A scale to measure hardness of a material
ASTM	American Society for Testing and Materials
EPDM	Ethylene-propylene-diene rubber
IIR	Butyl rubber
NBR	Nitrile rubber
NR	Natural rubber
PP	Polypropylene
SBS	Thermoplastic Styrene-Butadiene-Styrene elastomer
SEBS	Styrene-ethylene-butylene-styrene elastomer
TPU	Thermoplastic polyurethane elastomer
UL	Underwriter Laboratories
TPV	Thermoplastic vulcanizate
V1	Fire classification degree by UL
V0	Fire classification degree by UL
Additive	a substance added to plastic to improve its properties
Aliphatic	a carbon atom structure which does not contain aromatic rings
Block co-polymer	Co-polymer which monomers are organized as blocks
Co-polymer	Polymer that consists of two or more different monomers
Diol	Chemical compound which contains two hydroxyl groups
Elastomer	A polymer which can be stretched and returned to its initial form without permanent deformation
Hydrophobic molecule	A molecule which is repelled by water, usually nonpolar molecule

Hydroxyl group	A functional group with oxygen and hydrogen atoms (-OH)
Paraffin	common name for alkane hydrocarbons
Plasticizer	An additive to increase plasticity of the material
Vulcanized rubber	Rubber which chains are joined together with a chemical irreversible process

1 INTRODUCTION

This thesis was made for ABB Oy in co-operation with Trelleborg Industrial Products Finland Oy. The purpose of this thesis is to find a thermoplastic material, which can be used safely in conditions where it is subjected to oil and chemicals. This material must be RoHS compliant. ABB and Trelleborg Industrial Products Finland have been collaborating with material suppliers on finding a material which could be used in these conditions. In this thesis those materials gained from this collaboration will be tested in order to find out if they are potential gasket materials. Another objective is to find out which factors contribute to the swelling in thermoplastic elastomers' structure and in the geometry of the gasket.

The literature part of this thesis consists of introducing four material groups which have such properties that are required from the gasket material and considers their properties. These four groups are thermoplastic polyurethanes (TPU), styrene-ethylene-butylene-styrene (SEBS), thermoplastic vulcanizate elastomers (TPV) and co-polyester based elastomers. The literature part also discusses the factors which help estimate the amount of swelling based on the structure of the thermoplastic elastomer.

The experiment part of this thesis introduces immersion tests which have been used to determine oil resistance of the test materials. Six materials were tested, the names of the materials are confidential, they are coded to be Materials A, B, C, D, E and F. From these results, the best suited material for this purpose was elected. Also from the results, it was possible to determine dependence of swelling on volume, area, volume/area ratio and density of the sample.

2 SCOPE OF THIS THESIS

The scope of this thesis is to find a gasket material among thermoplastic elastomers which is oil resistant, has good tear strength and low hardness. This material needs to be RoHS compliant to replace the material currently used for gaskets, which is lacking this compliancy. The material also needs to have a fire classification minimum of V1.

Oil resistance of the material has to comply with UL 50 standard. The standard states, that gasket material shall not swell more than 25 % or shrink more than 1 % of its initial volume when it has been immersed in IRM 903 oil for 70 hours. (1) This will be tested according to UL 157 standard which gives instruction on how to perform the tests.

Good tear strength is important to this material, because when the gasket is used, a hole is made in the middle of the gasket. If the material has bad tear strength the gasket will tear too much when cables are pulled through it. The limit set to tear strength for this gasket material is 23 kN/m.

Hardness of the new gasket material is to be maximum 60 Shore A. This is for manufacturing purposes. This is the part of the requirements that make finding the gasket material difficult.

Another scope of this thesis is to find out which factors in the material's structure and gasket's geometry contribute to the swelling.

3 CLASSIFICATION OF MATERIALS

The materials that are concentrated on this thesis are thermoplastic polyurethane elastomers, styrene-ethylene-butadiene-styrene, thermoplastic vulcanizate elastomers and co-polyester blends. These materials were discovered to have best properties concerning the goals of this thesis. In this section, these materials are introduced.

3.1 Thermoplastic Polyurethane Elastomers

Thermoplastic polyurethane elastomers are very common elastomers. They can be processed with many different kinds of processing equipment and they can be made to have a large variety of physical properties. These are the reasons it is used in many different applications. The reason for its versatility is its unique structure. TPUs are used also in polymer blends. (2)

Thermoplastic polyurethane elastomers are block copolymers. The chain is made of two different kinds of segments; hard and soft segments. The hard segments of the material keep the material in its given form. The usage temperature is lower than polyurethane's glass transition point, so the polyurethane blocks stay hard during the usage of the product. When the product is warmed over its glass transition point, the material will soften and eventually melt, and it can be reshaped. (3)

In TPU's case, the hard segment has a carbamate group (shown in Figure 3.1) in the chain, which makes it polyurethane. The hard segments are made of polyisocyanate and chain extenders. The most popular polyisocyanate used in TPUs is 4,4-diphenylmethane diisocyanate, because its properties are good against its price. (4 p. 20) The most important chain extenders are linear diols, for example, ethylene glycol and 1,4-butanediol. When combined with diisocyanate, they form urethanes which are well crystallized and melt during thermoplastic processing, they do not decompose. Non-linear diols form urethanes which aren't well crystallized and thus have poor properties. (4 p. 21)

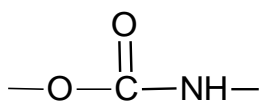


Figure 3.1. Carbamate group. (3 p. 374)

The soft segment can be either hydroxyl terminated polyester or hydroxyl terminated polyether. The soft segments are responsible for the low-temperature properties and the resistance to solvents.

There are two commercially important polyesters: polycaprolactones and aliphatic polycarbonates. Aliphatic polycarbonates produce a good hydrolytic stability. (4 p. 17) Especially, if colors and clarity are important to keep in the product even in sunlight the aliphatic hard segment is used (1). Technically important polyethers are poly(oxypropylene) diols and poly(oxytetramethylene) diols (4 pp. 17-18). Polyester based TPU's are cheaper than polyether-based ones (3 p. 375). The soft segments can also be made of mixtures of polyethers and polyesters. In these cases, the properties of the TPU formed can be a combination of properties. (4 pp. 17-18)

TPUs are made by reacting hydroxyl terminated polyester or polyether with an excess of aromatic diisocyanate to form a prepolymer, which is further reacted with a chain extender. The chemical structure of TPU is shown in Figure 3.2. (3 p. 376)

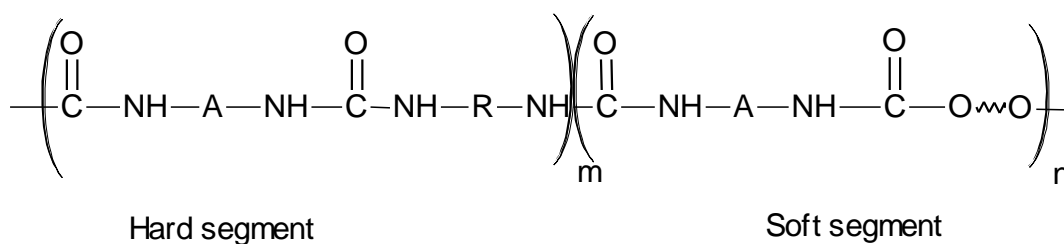


Figure 3.2. The chemical structure of TPU. A means aromatic diisocyanate structure, and O ~ O structure means polyester or ether structure. (3 p. 376)

3.2 Styrene-Ethylene-Butylene-Styrene Based Thermoplastic Elastomers

SEBS is a block copolymer which has stiff styrene blocks as intersections, beginning and ending ethylene-butylene elastomer blocks. This formation of blocks gives SEBS vulcanized rubbery like structure, where the crosslinks are not formed by a chemical process but physical process. When the material is heated, the intersection points melt, thus losing its strength, and the material can be reshaped. After cooling, the material has the same properties as before. The structure can be seen in Figure 3.3. (4 p. 47)

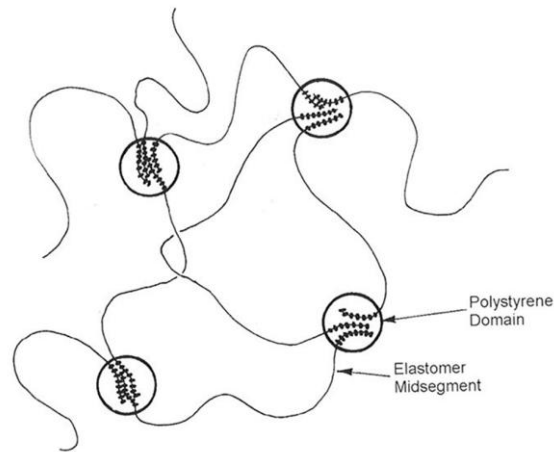
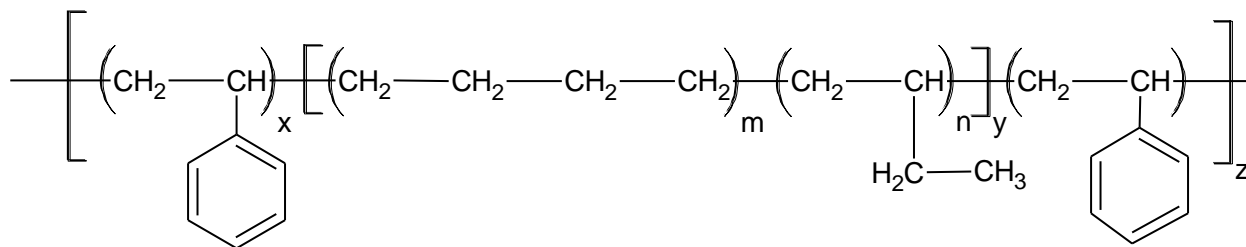


Figure 3.3. Phase structure of SEBS. Polystyrene domains act as intersections beginning and ending elastomer (Ethylenebutylene) blocks. (4 p. 47)

SEBS is made by using first sequential anionic living polymerization of styrene and butadiene to create unsaturated SBS polymer. This polymer is then hydrogenated. The result is a saturated polymer which chemical structure can be seen in Figure 3.4. (5; 6)



Poly(styrene-block-ethene-co-butane-block-styrene)

Figure 3.4. The chemical structure of SEBS. (5)

The structure has not got any double bonds (which defines a saturated structure), which is why SEBS has high thermal stability naturally. If stabilizers are used, the thermal stability can be increased and UV-resistance and aging properties improved. (7)

3.3 Thermoplastic Vulcanizate Elastomers

TPVs are blends of vulcanized elastomer and thermoplastic plastic. When these two are combined, the result is a material which behaves as thermoplastic elastomers do. The elastomer is responsible for the elasticity of the material and the plastic is responsible for the material's ability to be reformed easily. Picture of the structure is in Figure 3.5. The ideal case is that small rubber particles are dispersed evenly in to the plastic and stay that way during the lifecycle of the product. This way the properties of the material don't vary through the material. TPVs are manufactured by using a technique called dynamic vulcanizing. Using this method, better properties are obtained than if the used material would be block copolymer type. The difference is due to the fully vulcanized elastomer particles in TPVs, and their ability to form a network of vulcanized elastomer during processing of the material. The better properties include better hot oil resistance which is important for the material looked for in this thesis. Different properties can be achieved depending on the ratio of plastic and elastomer. (4 p. 146)

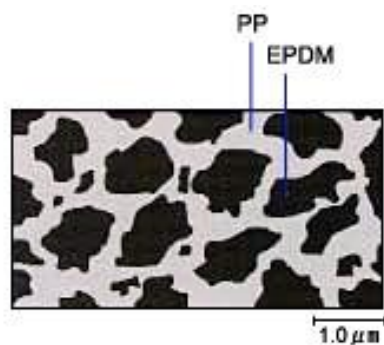


Figure 3.5. The structure of polypropylene (PP)/ethylene-propylene-diene (EPDM) TPV. As can be seen from the picture, the rubber (EPDM) particles are dispersed evenly in PP matrix. The two materials are mixed, not reacted with each other. (8)

Polyolefin based thermoplastic vulcanizates are TPVs based on polyolefin plastics, (for example ethylene-propylene-diene rubber and polypropylene). Typical polyolefins are polypropylene and polyethylene.

The properties of the material change according to ratio of the materials. Let's look at EPDM and polypropylene for example. When the percentage of the matrix (PP), is increased, the modulus, hardness, tension set and strength increase also. When the percentage of the matrix is more than 30 but less than 50 the strength of the material increases rapidly, but outside of those limits, the change is only slight. It has also been tested that using oil extension and carbon fillers the properties are not influenced. (4 pp. 146-154)

Another kind of rubber which can be mixed with polyolefins is diene rubbers. Commercially most important diene rubber used in TPVs is natural rubber (NR). These mixtures have good tensile properties and a bit better thermal stability than NR alone. Mechanical properties vary depending on the hardness of the mixture. (4 p. 154)

Another group of TPVs are mixtures of butyl rubber (IIR) and polypropylene. These mixtures have very low permeability for water and air. Different properties can be achieved if some other rubber (neoprene for example) is used together with IIR and PP. The properties of the new three compound material differ with a wide range depending on the ratio of the rubbers. The properties can be rather surprising, because the new properties can be smaller, or larger than either of the original rubbers' properties, not necessarily average of the two. (4 pp. 155-156)

Nitrile rubber (NBR) and polyamide mixture thermoplastic elastomer can be manufactured to have different kinds of properties. The properties, which the material will have, depend on the manufacturing of the material. Nitrile elastomers are divided into two groups; those which can self-cure (cure at elevated temperatures without a curative) and those which need a curative. Using curatives increases tensile strength and hardness, but decreases tension set and the percentage the material has elongated before breaking. The improvement in NBR-polyamide's properties is also due to some curatives' ability to cause gel formation in the elastomer. Because of the gel, the properties improve. Some curatives also react with the polyamide and cause some crosslinking between the polyamide and the elastomer causing better adhesion between the phases. This results to NBR-polyamide's rater rare ability to have widely variable tension set values, where usually (like in the case of EPDM and PP compounds) the curative reduces those values. (4 p. 158)

3.4 Co-polyester Based Elastomers

Polyester thermoplastic elastomers generally mean segmented poly(ether ester) block copolymer with alternating random-length segments of long-chain or short chain oxyalkylene glycols joined by ester links such as tetramethylene terephthalate. The polyester part of the chain is a hard segment and the soft segments are from aliphatic polyether glycols. The elastomeric segments are crosslinked together by the hard segment's ability to crystallize. The crystalline segments hold the elastomeric parts together and are responsible for the material's ability to be reformed. (4 p. 183) The phase structure can be seen in Figure 3.6.

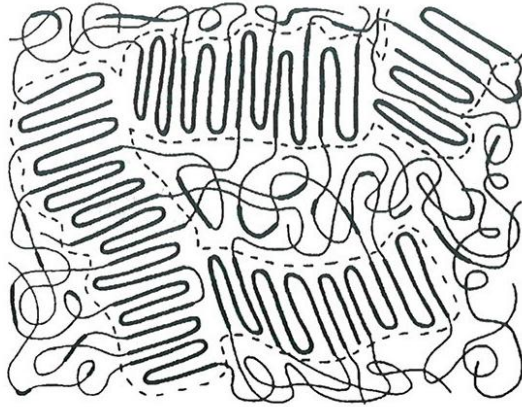


Figure 3.6. Phase structure of polyether-polyester block copolymer. Hard (polyester) segments can be seen as denser parts of the chain, which are crystalline. The amorphous (polyether) segments are the chains which appear to be randomly spread in the picture. (4 p. 183)

Co-polyester based elastomers are a good group to focus on keeping in mind the objective of this thesis because the achievable hardness range is wide. By adjusting the ratio of the hard and soft segments different kinds of material can be achieved. If there is more polyester in the material than polyether, the material is hard and has properties which are closer to those of polyester. If, on the other hand, the material contains more polyether segments (soft segments) the properties of the material are closer to elastomer's properties. The general chemical formula of co-polyester based elastomers can be seen in Figure 3.7. (4 p. 183)

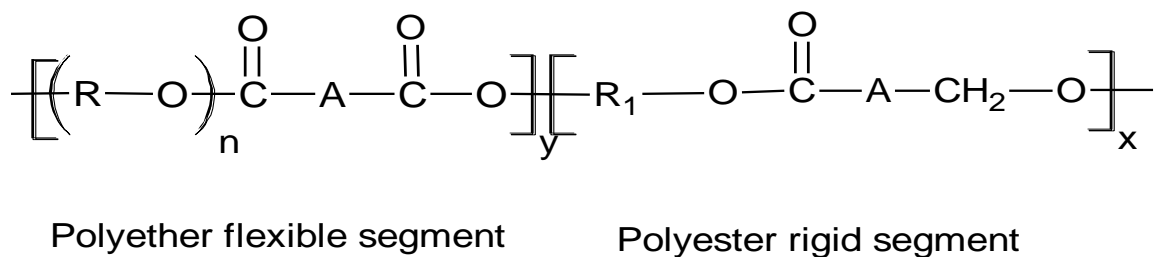


Figure 3.7. The general chemical formula of Polyester based elastomer. R and R₁ means aliphatic chain, A-aromatic ring, n=14-28; y=1-3;x=3-40. (9 p. 582)

Different properties can be achieved through modification of the hard and soft parts of the chain. For example, when the object is subjected to tearing, an isophthalic acid is a better choice than terephthalate for the hard segment. Tear strength becomes higher, but

modulus gets lower. The same kind of modification is possible for soft segments as well.

The most common commercial co-polyester based elastomer is built with a flexible segment of poly(tetra-methylene oxide) and rigid segment of poly(butylene terephthalate) (9 p. 582).

4 CHEMICAL RESISTANCE, HARDNESS AND MECHANICAL PROPERTIES OF THERMOPLASTIC ELASTOMERS

This section contains an overview on chemical resistance of those thermoplastic elastomers which are tested in this thesis. The chemical resistance properties of a thermoplastic elastomer are different for each elastomer, and that is why each elastomer's properties need to be analyzed separately.

4.1 Thermoplastic Polyurethane Elastomers

Thermoplastic polyurethane elastomers have a good resistance against nonpolar solvents. This is because in both soft segment alternatives (polyester and polyether) there are polar groups in the chain (9). Only slight swelling is noted, when TPU is subjected to nonpolar solvents under elevated temperatures. Some polar solvents, on the other hand, are able to seriously damage or even dissolve TPU. (4 p. 34)

Usually, TPUs can resist pure mineral oils, diesel oils and greases very well, but some greases and technical oils can damage them in high temperatures. This is because of the additives used in TPUs. Therefore it is always wise to test these chemicals' affect on TPU under the conditions the material is intended to be used. (4 p. 34)

Chemicals, which will cause swelling in TPU, are chlorinated hydrocarbons and solvents which contain aromatic structures (toluene for example). Paraffin types of solvents (kerosene for example) don't cause a lot of swelling. (10)

Depending on the structure of the TPU, the swelling can appear in different degrees. If TPU's structure has hydroxyl terminated polyether as the soft segment, the swelling will be greater than if the soft segment was hydroxyl terminated polyester. Also, hard polyurethanes will swell less than soft ones. (4 p. 34)

Polyester-based TPU's have better high temperature stability and oxidative stability. Polyether-based, on the other hand, have better flexibility in low temperatures and a better hydrolytic stability. (3 p. 375)

Hardness range of TPUs can vary from 60 Shore A to 70 Shore D (4). The properties of the material are different depending on the structure of the polymer chain, even if the hardness is the same. Polyester based TPUs have a better oil resistance and they are tougher than polyether based ones, but polyether ones have better hydrolytic stability and low temperature flexibility. (10 p. 442)

Generally, when the hardness increases, hydrolytic stability improves, because the ratio of the hard segments increase and the hard segments are hydrophobic. Acids and bases dilute TPU. (4 p. 34)

The differences in properties between ester and ether based TPU's are shown in Table 4.1.

Table 4.1 Different properties of TPU's soft segments. ++ = Excellent, + = Good, 0 = indifferent. (3 p. 32)

Property	Ester	Ether	Etherester
Tensile & Tear Strength	++	0	+
Abrasion Resistance	++	0	+
Weathering	+	0	+
Low swelling in Fuels /Oils/Greases/Water	++	0	+
Low Temperature Flexibility	0	+	+
Fungus Resistance	0	++	+

The mechanical properties of TPU are good. It has an excellent tear resistance, abrasion resistance and wear resistance. It also has high tensile strength, but this depends on the ratio between soft and hard segments. (11 p. 13) Some of TPU's mechanical properties are given in Table 4.2.

Table 4.2. Some mechanical properties for TPU. (12)

Property	Typical range
Hardness (Shore)	60 Shore A to 70 Shore D
Tensile Strength (MPa)	1.31 - 50.6
Elongation at break (%)	6 - 720

4.2 Styrene-Ethylene-Butylene-Styrene Based Thermoplastic Elastomers

Typical characteristics of SEBS elastomers include wide hardness range, very good tear resistance, chemical resistance to acids, bases and detergents and flame retardancy (13). Due to the structure of SEBS (the lacking of double bonds), it has very good properties without the addition of stabilizers and such. It's resistance to hydrolysis is very good as well as most dilute alkali and acids. If high resistance of strong acids is necessary, fillers must be added. Resistance to vegetable fats is moderate and saturated animal fats poor. Resistance is also poor against gasoline, fuels, lubricating oils and many solvents. Resistance of SEBS is good against alcohols and glycols. (7)

SEBS also has a good resistance against UV-light, oxygen and ozone. There are some mechanical properties given in Table 4.3.

Table 4.3 Typical range of properties for SEBS. (14 p. 112)

Property	Typical range
Hardness (Shore)	35 Shore A to 40 Shore D
Tensile Strength (MPa)	6.5 - 11.0
Elongation at Break (%)	425 - 800
Tear Strength (kN/m)	28 - 78.8
Service Temperature (° C)	-70 - 80

4.3 Thermoplastic Vulcanizate Elastomers

The properties of TPV depend on the materials chosen to form the TPV. There are also other things which have an effect on the properties. The most important aspect is the proportions of the materials used in the mixture. If more rubber is added, the material gains more flexible properties and if more plastic is added the materials properties go toward the properties of the plastic. Also, the particle size of the elastomer has an effect on the properties for example the mechanical properties improve. The compatibility between the plastic and rubber particles is usually poor and compatibilisers must be used. (15 pp. 107-108)

In the case of NBR rubbers, the more the rubber contains acrylonitrile the less the material swells when subjected to oil. (4 p. 159)

Plasticizers are usually used in NBR-polyamide mixtures to improve fabricability and soften the material. Usually, the melting point of the polyamide decreases when plasticizers are used, and so does the viscosity of the material. Decrease in viscosity of the polyamide may lead to the melt polyamide to crystallize and therefore form crystals which have more perfect structure. Tensile strength usually decreases when plasticizers are used. (4 p. 160)

Fillers can also be used to alter the properties of the NBR-nylon TPV. Clay can be used to fill the TPV, it has only a small influence on hardness, stiffness and strength, but it decreases extensibility and Young's modulus. Fillers also reduce thermoplasticity and thus fabricability. Used together with plasticizers thermoplasticity and extensibility can be regained. (4 p. 161)

4.4 Co-polyester Based Elastomers

Co-polyester based elastomers have very wide use purposes. They are exceptionally good in applications which demand high toughness, and flex resistance with heat and chemical resistance. Oil resistance is great. These are reasons for considering this ma-

terial for this thesis. However, the hardness creates a problem, because commercially available co-polyester based elastomers' hardness is ranging from 40 to 72 Shore D (40 Shore D is roughly around 85 Shore A). The purpose of this thesis is to find a material which hardness is less than 60 Shore A. (14)

Co-polyester based elastomers need to contain antioxidants, because without them they will degrade in air. The process is based in free radicals and will eventually form formic acid. Other stabilizers that will be necessary are a free radical trap, an agent to decompose hydroperoxides and an agent to trap formaldehyde. (16)

Water can also be a problem for these materials. They are permeable to water and can degrade by hydrolysis at elevated temperatures. Hydrolytic stability is better than with TPUs which have polyesters as the soft segment. Also, a problem for these materials is the insulation properties, because they do not insulate electricity as much as they should in order to be used as insulators. (14 p. 113)

Some mechanical properties are in Table 4.4.

Table 4.4. *Mechanical properties of co-polyester based elastomers.* (14)

Property	Typical Range
Tensile Strength (MPa)	25 - 38
Elongation at Break (%)	350 - 450
Tear Strength (kN/m)	122 - 154
Service Temperature (° C)	-50 - 150
Hardness (Shore)	85 Shore A – 72 Shore D

4.5 Comparison of Properties

Comparison of the material properties is difficult, because each material has a wide range of properties. SEBS is the only material which properties can be said to be at a certain range. TPU and TPV's properties depend much from the structure of the materials. TPU can have either polyether or polyester (of the mixture of these two) as the soft segment and TPV's properties depend on the materials chosen for the rubber and matrix phases.

In Table 4.5 there is a comparison between these materials and important properties keeping in mind the scope of this thesis. TPVs are not included as the properties of them vary too widely, which makes comparison hard.

Table 4.5. Comparison of material groups' properties relevant to this thesis. ++ = Excellent, + = Good, 0 = Indifferent, - = Poor.

Property	TPU	SEBS	Co-polyester
Oil resistance	++	-	++
Hardness (Shore A- Shore D)	60 - 78	35 - 40	85 - 72
Hydrolytic stability	+	++	0
Tear resistance	++	++	++
Tensile strength (MPa)	1.31 - 50.6	6.5 - 11	25 - 38

In Table 4.5 it can be seen, that TPU is a good candidate for the gasket material, because all the key properties are acceptable. However, in this table the properties of TPU are the best properties there are, without mentioning which kind of structure the TPU has in each case. It can be, that the kind of TPU with all good properties is hard to find. In this thesis the material looked for needs to be relatively soft, and soft TPUs have poor hydrolytic stability. It would be wise to compound it with some other material, which has good hydrolytic stability, for example SEBS. Co-polyester would also be a good choice if requirements for hardness of the material could be loosened a bit.

5 MATERIALS

In this thesis, the materials are coded as A, B, C, D, E and F for product development purposes. The key is not available in the public versions of this thesis. Five of these materials are candidates for the new material and one is the material used at the present moment to manufacture the gaskets. Information of this chapter is taken from each material's individual datasheet. Because the materials are confidential, the datasheets do not appear in the bibliography.

5.1 Material A

Material A is the material used currently in the gaskets. It belongs to the group of SEBS materials. Its color is black, it has excellent weather resistance and moderate chemical resistance. It is 100% recyclable. It has two special features; the compound has been developed to be flame retarded at 1,5 mm thickness to meet UL94 V-0 requirements with a degree of oil resistance.

The material can be processed with conventional processing techniques such as injection molding and extruding. In Table 5.1 there are some typical properties according to the data sheet of the material.

Table 5.1. Properties for material A as given by its datasheet

Property	Typical value
Hardness (Shore A)	50
Specific Gravity (g/cm ³)	1.24
Tensile Strength (MPa)	3.3
Tear Strength (N/mm)	15
Elongation at Break (%)	270
Flammability	V-0

This material has hardness of 50 Shore A which meets the requirements well. The tear strength is less than required from the new material. This material is not RoHS compliant.

5.2 Material B

Material B is Thermoplastic vulcanizate. Its color is white and it can be molded by extrusion and injection molding. Properties for material B are in Table 5.2 as given by its data sheet.

Table 5.2. Properties for material B as given by its data sheet.

Property	Typical value
Hardness (Shore A)	55
Specific Gravity (g/cm ³)	1.25
Tensile Strength (MPa)	6.55
Flammability	V-0
Elongation at Break (%)	400

The data sheet did not give tear strength for material B. The hardness of the material is suitable for the purposes of this thesis. This material is RoHS compliant.

5.3 Material C

Material C is a gray colored SEBS material. Material C is suited to conventional forming techniques such as injection molding and extrusion. Properties of the material are in Table 5.3.

Table 5.3. Properties for material C as given by its data sheet.

Property	Typical value
Hardness (Shore A)	55
Specific Gravity (g/cm ³)	1.27
Tensile Strength (MPa)	8.69
Elongation at Break (%)	790

This material's nominal hardness is 55 Shore A. This is compliant to the gasket material's requirements. In addition, this material has been developed to be flame retarded at 1,5 mm thickness to meet UL94 V-0 requirements. Material C is RoHS compliant.

5.4 Material D

Material D is marked in its datasheet to belong to the group of thermoplastic polyurethane elastomers. Actually, it is a mixture of TPU and SEBS. Its appearance suggests that, too. It is white material with black lines going through it. Because it is a mixture, it has best of both properties. According to the datasheet Material D has a good abrasion resistance, oil resistance and scratch resistance. This material is also RoHS compliant, but it does not have fire classification. Material D can be formed by extrusion and injection molding. In Table 5.4 there are some properties for Material D.

Table 5.4. Properties for material D as given by its datasheet.

Property	Typical value
Hardness (Shore A)	55
Specific Gravity (g/cm ³)	1,02
Tensile Strength (MPa)	14,7
Elongation at Break (%)	630

5.5 Material E

Material E's datasheet states, that Material E has a good resistance to acids, bases and alcohols. It is easily colored though in these tests the material was black. Its resistance against hydro-carbons (oils for example) is moderate. Material E is also a SEBS material and can be formed by injection molding, extrusion and blow molding. It has two fire classifications, for 1,5 mm sample V1 and for 3,0 mm sample V0, both classifications were done by UL 94 standard. Material E is also RoHS compliant. Tear strength and hardness are acceptable for this purpose. More information about its properties can be seen in Table 5.5.

Table 5.5 Properties for material E as given by its datasheet.

Property	Typical value
Hardness (Shore A)	60
Specific Gravity (g/cm ³)	1,2
Tensile Strength (MPa)	4,5
Elongation at Break (%)	400
Tear Strength (kN/m)	23

5.6 Material F

Material F is improved version of Material B. It is also a white thermoplastic vulcanizate elastomer. According to its datasheet, good forming techniques are extrusion and injection molding. The datasheet says nothing on RoHS compliancy. Material F has a fire classification of V0 for 3,0 mm thick sample, tested according to UL 94. More of its properties can be found from Table 5.6.

Table 5.6. Properties for material F as given by its datasheet.

Property	Typical value
Hardness (Shore A)	55
Specific Gravity (g/cm ³)	1,25
Tensile Strength (MPa)	5,85
Elongation at Break (%)	420

6 THE EFFECT OF OIL ON ELASTOMERS

Elastomers may experience swelling when subjected to solvents. When considering the material's ability to swell, it must be remembered to look at the whole picture before any assumptions are made. It is important to remember that besides the material, also plasticizers, fillers, the amount of crosslinking and chemical structure affect the swelling process. The swelling is caused by diffusion of the fluid into the structure of the elastomer. The amount of swelling is influenced by vulcanization degree, concentration of the solvent, time the elastomer is subjected to the fluid and temperature. (17) (18 p. 128) In this section the swelling phenomena is considered.

6.1 Solubility Parameter

Whether or not a material is likely to swell in a known liquid can be determined using the solubility parameter. If the solubility parameter of the liquid is close to the solubility parameter of the elastomer, the elastomer is likely to swell by that liquid. Solubility parameters are close to each other for those materials that have similar chemical structure. For example, hydrocarbon rubbers are soluble in hydrocarbon solvents, such as petrol, but they are insoluble to polar liquids such as alcohol. A concrete example of this is NBR rubber. The key element in NBR rubber is the amount of acrylonitrile: when the portion of acrylonitrile changes, the solubility parameter of the NRB changes. In NBR's case, when the solubility parameter is more than 1.5 points apart from the solvent's parameter, the material swells less than 25 %. Usually, NBR's solubility parameter (δ) varies from 9.0 to 10.5, so if the swelling limit is 25 %, it swells less when the solvent's solubility parameter is 7.5 to 8, as most lubricant oil's parameter is. (18 pp. 148-149) (19 p. 523)

Mineral oils have the ability to swell nonpolar elastomers large amounts. They do not however swell polar elastomers. The amount of swelling is affected by the amount of aromatic hydrocarbons in the solvent. (20 p. 62)

Solubility parameter can be difficult to determine for complex compounds as oils. For oils, there is a constant that will help estimate the solubility parameter, aniline point. Aniline point is a temperature in which aniline and oil are completely miscible. The aniline point must be converted to Kauri butanol number (standardized measure of solvent power for a hydrocarbon solvent) first and then the Kauri butanol number must be converted to solubility parameter. (21)

6.2 Hydrophobic Elastomers

Polymers can be categorized into two categories. In the first category there are polymers which swell in water, also known as hydrophilic polymers. The other category is for those polymers which swell only in organic, hydro-carbon solvents. Elastomers belong in this category. These elastomers are known as hydrophobic polymers. These polymers tend to swell, when subjected to organic solvents and some other kinds of fluids, for example petrol. The swelling can be observed as changes in the measurements of the sample, weakened properties, migration of its additives or degradation of the sample. Elastomers can also shrink when subjected to solvents, because some parts of the elastomer (additives for example) may be leached by the fluid. (18 p. 128) (22) (17) (20 p. 62)

6.3 Test Oils

There are oils, which are only used to test oil induced swelling in elastomers. The ASTM oils are designed so, that they resemble commercial oils giving the same kind of influence on the elastomers as the commercial oils do. (23 p. 70)

In this thesis IRM 903 oil was used. It is a naphthalene based mineral oil as well as its sister oil IRM 902. IRM 902 is medium swelling reference oil. It swells the samples less, than IRM 903 which is labeled as high swelling reference oil. In Table 6.1, there are properties for both reference oils. (24)

Table 6.1. Properties of reference oils IRM 902 and IRM 903. (25)

Property	IRM 902	IRM 903
Aniline point, °C	93.0 ±3.0	70.0±1.0
Viscosity-gravity constant	0.865±0.005	0.880±0.005
Naphtalenics Cn %	min 35	min 40
Paraffinics Cp %	max 50	max 45

As can be seen from Table 6.1, IRM 903 has higher naphthalene content than IRM 902. IRM 903 is used in the tests done for this thesis, because it can be best compared to typical hydraulic oils. IRM 903 has more naphtalenics in it than IRM 902. Naphthalene is a hydrocarbon (it consists of two fused benzene rings), so it is not very polar substance and thus it swells nonpolar elastomers (26). This is why IRM 903 is “stronger” solvent for nonpolar elastomers. Also, the aniline point correlates with the swelling, the lower aniline point the oil has, the more severely it will damage the material (23 p. 70). This means that IRM 903 swells samples more than IRM 902.

7 TESTING OF OIL INDUCED SWELLING ON THERMOPLASTIC ELASTOMERS

In this thesis, tests were made to find out which factors affect oil induced swelling of thermoplastic elastomers. First test was immersion test in order to determine the amount of swelling of each material chosen for this thesis. From the information given by these tests a pattern of swelling for each material is determined. Also density's affect on swelling was pondered. This section introduces the tests done in order to achieve those goals.

7.1 Oil Resistance Test

The first test done was an oil resistance test. This test aimed to measure the volume change of the samples. When elastomeric materials are immersed in oil, they can experience some swelling, shrinking or parts of them can dissolve in the oil. This test was made according to UL 157 standard, which describes how oil immersion tests are to be carried out (27).

Tests were made in three phases. In the first phase there were six materials and two specimen geometries. In the second phase, there were three specimen geometries, and four materials left. One material was discarded based on results from the first phase and second material was discarded due to too high hardness of the material. In the third phase real gasket geometries were used in the tests. Only three materials were tested in this phase, because of logistical problems of one material.

7.1.1 Specimens

The materials are coded for production development purposes, the materials used in the tests were A, B, C, D, E and F. In the first phase all materials were tested. In the second phase Materials A, C, E and F were tested and in the third phase only Materials A, C, E were tested. The phase separation is based on the geometry of the samples.

The first phase of the tests

The first samples were rod shaped as seen in Figure 7.1. From each material two thicknesses were tested in order to find out if the thickness of the material affects the percentage of the volume change. Normally, three parallel samples were used and the total number of specimens tested from each material was 6. In some cases the tests were done again, so the number of samples can vary, but the minimum number of samples was always 6.

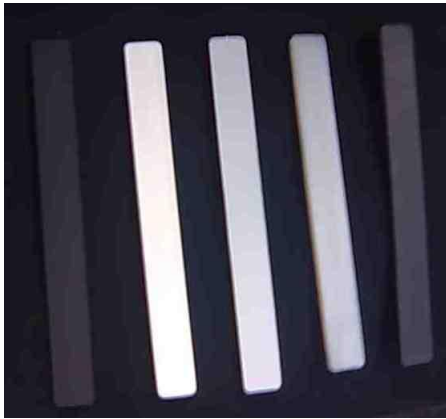


Figure 7.1. Specimens tested in the first phase of tests. Materials from left: A, B, C, D and E.

The measurements of the rods are in Table 7.1. Volume and area of each sample were measured, so that the effect of samples geometry on swelling could be determined.

Table 7.1. Measurements of the test samples of the first phase of the tests.

Thickness (mm)	Length (mm)	Width (mm)	Area (mm ²)	Volume (mm ³)
1.5	125	13	3641	2426
3	125	13	4047	4852

Second phase of the tests

The second test samples were square shaped. Measurements are on Table 7.2. Again, the area and the volume were measured so that the dependence between volume, area, volume/area (V/A) ratio and swelling can be determined. Each sample thickness was tested three times, but again some samples may have been tested more than three times. Always the minimum number of tested samples per thickness was three. Pictures of the samples are in Figure 7.2

Table 7.2. Measurements of the samples used in the second phase of the tests.

Thickness (mm)	Length (mm)	Width (mm)	Area (mm ²)	Volume (mm ³)
0.8	25.4	25.4	1352	509.9
1.5	25.4	25.4	1420	956.2
3	25.4	25.4	1564	1912

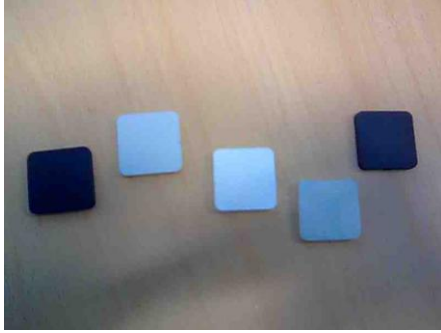


Figure 7.2. Test samples used in the second phase of the tests. Test samples from left: A, D, B, C and E.

In the second part of the test, the materials used were A, C, E and F. The materials B and D were ruled out from this round of the tests because the results from the first test were unsatisfactory.

Third phase of the tests

In the third phase of the tests the samples were real products manufactured from the test materials. Product 58915394 is in Figure 7.3 and gd-27_103538 is in Figure 7.4.



Figure 7.3. Test sample 58915394 which were used in third phase of the tests.

The shape of the specimen caused large air bubbles to stay on the surface of the material during weighing in water and they had to be carefully removed. This caused some inaccuracy if all bubbles were not detected.



Figure 7.4. Test sample gd-27_103538, which were used in third phase of the tests.

Measurements of these test samples are in Table 7.3.

Table 7.3. Measurements of samples used in third phase of the tests.

Sample name	Area (mm ²)	Volume (mm ³)
gd-27_103538	5003	6934
58915394	4335	6337

7.1.2 Apparatus

The oil used was ASTM test oil IRM number 903, as required in the standard. The test required a balance, which made it possible to measure the samples' weight in air as well as in water. Balance Precisa 500 M-2000 C was used, seen in Figure 7.5.



Figure 7.5 Precisa 500 M- 2000 C balance, which was used to measure the weight of the samples. The balance has a hook under it, so it was possible to weigh the samples.

The samples were hung from a thin wire hook to measure the sample's weight. The hook is shown in Figure 7.6. Things also used in this experiment were alcohol to clean the samples and some water to do the weighing in.



Figure 7.6. Weighing in air. Wire hook was attached to the sample and then the hook was attached to the hook of the balance in order to weigh the sample.

7.1.3 Procedure

In the beginning of the test, each sample was weighed. The weighing happened in air (Figure 7.6) and in water (Figure 7.7). Before weighing in water, the sample was rinsed with alcohol and water to make sure no other substances influenced the result. While measuring in water, it was made sure that no air bubbles were attached to the sample as they affect the weight. Each sample was weighted in water three times and the average value was used, to be sure that no air bubbles affected the final results.

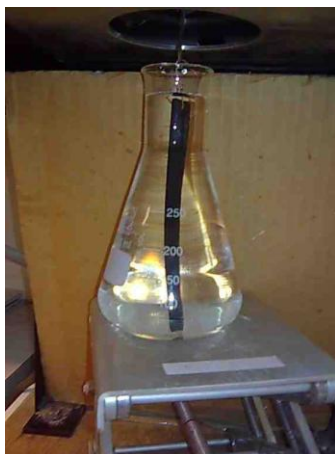


Figure 7.7. Weighing in water. The water container was cleared from bubbles. The sample was not to touch the walls or the bottom of the container.

After the measuring and weighing, the samples were immersed in a decanter glass which was filled with oil. Each glass had from three to four samples at a time. It was important that none of the samples touched the walls of the container or other samples. This was because it was important that the oil could affect the sample from all directions. The samples remained in the hooks they were weighed with and with those hooks the samples were hung in the oil as can be seen from Figure 7.8. The samples stayed in oil for $70 \pm \frac{1}{2}$ hours in the room temperature of 23 ± 2 ° C.



Figure 7.8. The samples were hung from the wire hooks and immersed in oil.

After the samples had stayed in the oil for the required time, they were taken out. Excess oil was wiped from the surface of the sample, so that it did not drip. After taking the sample out of the oil, it was weighed in air within 30 seconds as the standard ordered. Next, the sample was rinsed in alcohol and water and then weighed in water. According to the standard, the measuring in water was supposed to take place within 60 seconds from the removal from the oil. This however proved to be difficult, as the weighing in water had to be made three times for each sample (to remove the effect of the bubbles). In the end, the weighing in water took place within three minutes of the removal from the oil, and measuring the sample within 4 minutes from the removal.

7.1.4 The Equations

Immersion test was made in order to determine the percentage of the volume change of the samples caused by the oil. According to standard UL 157 the volume change can be counted from the following equation:

$$\Delta V\% = \frac{[(M_3 - M_4) - (M_1 - M_2)] * 100}{M_1 - M_2} \quad [1].$$

In equation [1]:

ΔV is the volume change of the sample induced by the oil

M_1 is the weight of the specimen before the test on hook on air

M_2 is the weight of the specimen before the test on hook in water

M_3 is the weight of the sample on hook on air after the test

M_4 is the weight of the sample on hook in water after the test

Equation [1] states that volume change can be counted from the weight differences of the sample weighed in air and water before and after the test. The limit for acceptable volume change is 25 % according to UL standard 50.

7.2 Density Measurement

Density was measured from five materials (A, B, C, D and E) in order to determine the affect of density in the amount of swelling.

7.2.1 Specimens

The specimens were 3,0 mm thick samples which were used in the second phase of the immersion tests. In the test, two specimens of each material were used, because the weight of a single specimen was too low.

7.2.2 Apparatus

The measurements were done with Wallace density measuring device which is presented in Figure 7.9. The device consists of a balance on top of which was a black container. The container had water in it.



Figure 7.9. Wallace density measuring device used in these measurements. Weighing in air happened on top of the black container. Weighing in water happened inside the container.

7.2.3 Procedure

At the beginning, samples were placed on top of the black container. The device measured the weight of the samples first in air. After the machine was done measuring the weight of the samples, the container was opened and the samples were placed in the water inside the container. It was very important, that no air bubbles were allowed under the water on top of the samples, because this affected the measured weight of the sample and consequently the measured density. The device gave out the density outright.

8 RESULTS

8.1 Immersion Test Results, First Phase

In the first phase of the tests the specimens were bar shaped samples with thicknesses of 1,5 mm and 3,0 mm.

The first material tested was Material B. As can be seen from Figure 8.1 the material swells more than the allowed 25 % with both tested thicknesses (1,5 mm and 3,0 mm) in the bar shaped sample geometry. The average value of the swelling of 1,5 mm thick samples was 52,85 %, which is more than double the amount which was approved by UL 50. Also the average increase in volume of 3,0 mm thick samples was too much, 29,09 %. This material was ruled out of the second phase of tests, because these results were unsatisfactory.

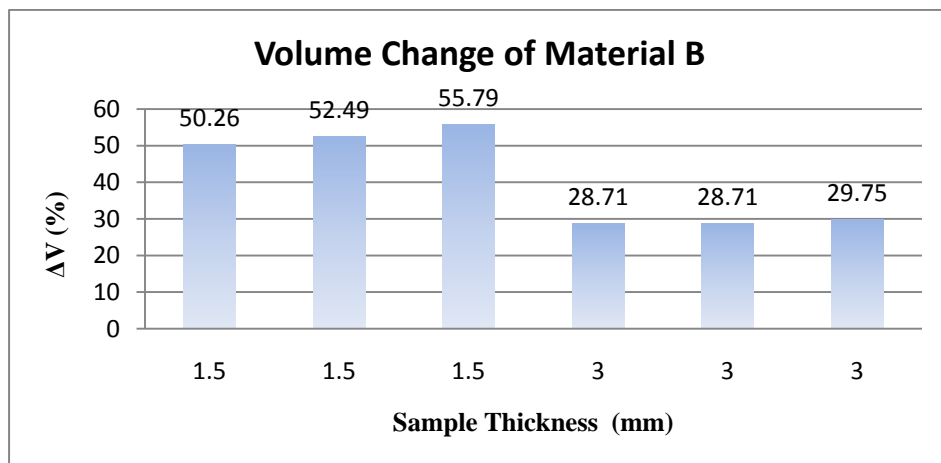


Figure 8.1. Results from immersion test of Material B from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material.

The second material tested was Material E. This material showed better performance in oil swelling tests than the previous Material B. These results can be seen in Figure 8.2.

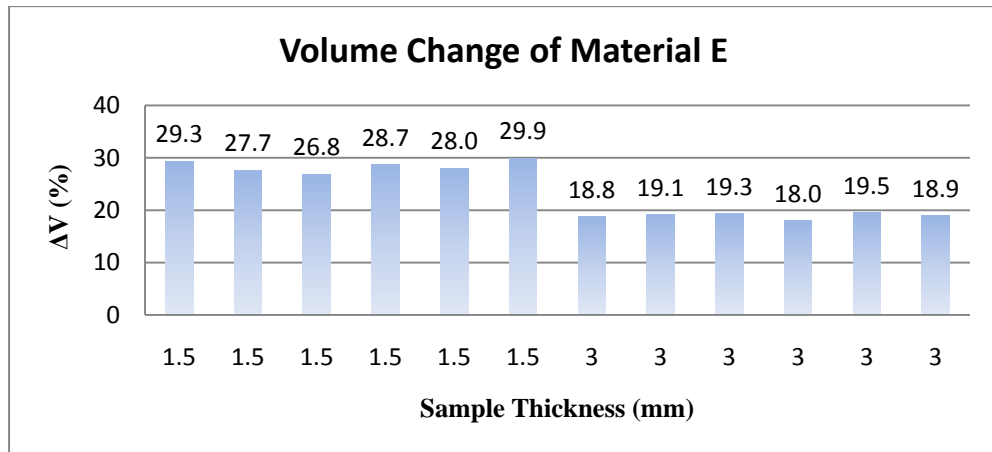


Figure 8.2. Results from immersion test of Material E from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material.

The average swelling of a 1,5 mm thick sample was 28,40 % and of a 3,0 mm sample 18,93 %. The 3,0 mm thick sample fits well into the 25 % limit which UL 50 sets and the 1,5 mm result is close to being acceptable. Two sets of samples were tested from this material, all together 6 samples from both sample geometries. Both these samples will be tested again in the second phase of the tests.

Third material tested was Material C. Results can be seen in Figure 8.3. 3,0 mm thick samples have only swelled the average of 23,10 % and thus it qualifies to UL 50. However, the 1,5 mm thick samples have the average swelling of 41,51 % which isn't close to the approved maximum swelling of 25 %. Two sets of samples were tested from this material, all together 6 samples from both sample geometries. This material will be tested again in the second phase of the tests.

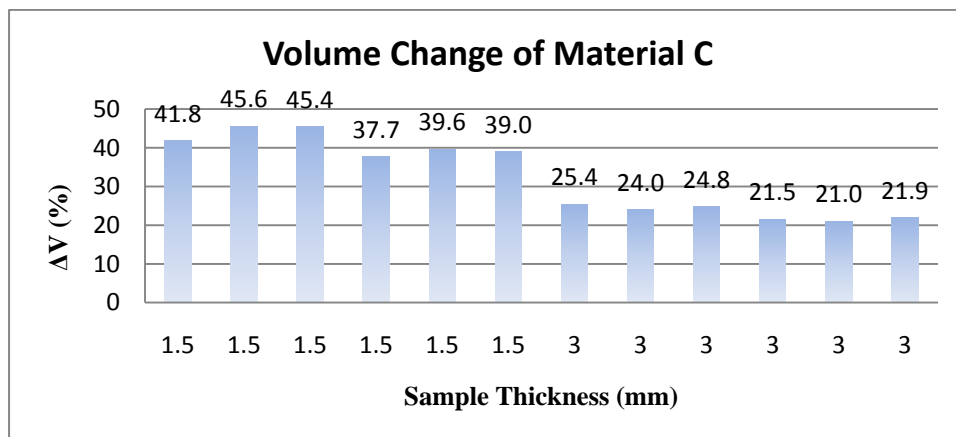


Figure 8.3. Results from immersion test of Material C from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material.

The fourth material was Material A. This material performed well in the immersion test. The results can be seen in Figure 8.4. The average swelling of 1,5 mm thick samples was 31,85 %, which is a bit over the UL 50 approved limit of 25 %. On the other

hand, the swelling average of 3,0 mm thick samples was 19,88 %, which is well within the limits. Two sets of samples were tested from this material also. This material will be tested in the second phase of the tests.

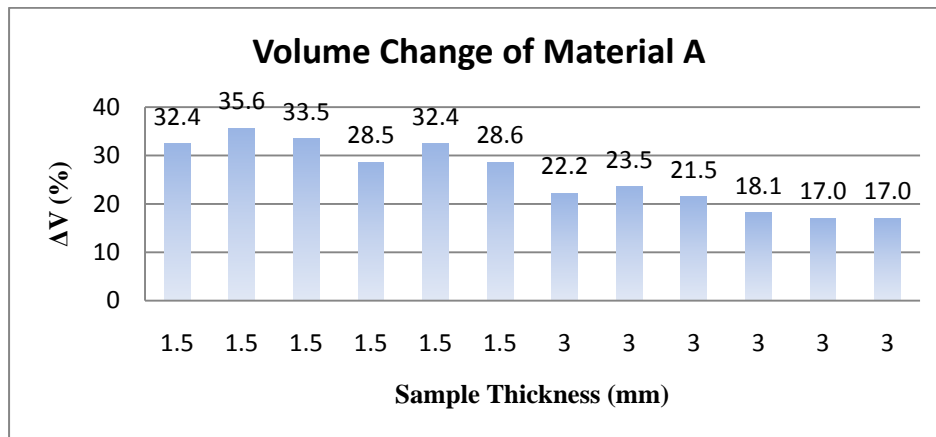


Figure 8.4. Results from immersion test of Material E from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material.

The fifth material tested was Material D. The results are in Figure 8.5. These results were the best ones from all the materials tested.

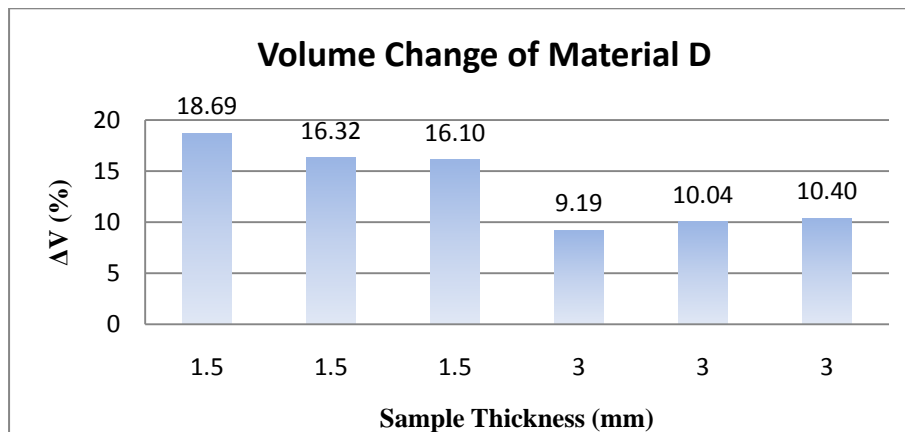


Figure 8.5. Results from immersion test of Material D from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material.

The average swelling of 1,5 mm thick samples was 17,04 %, which makes this the only material so far qualifying the UL 50 limit in 1,5 mm thick samples. The results of the 3,0 mm thick samples were also good, average swelling was 9,87 %. However, this material does not have a fire classification, so it will not be tested again in the second phase of the tests.

The last material tested was material F. The results are in Figure 8.6.

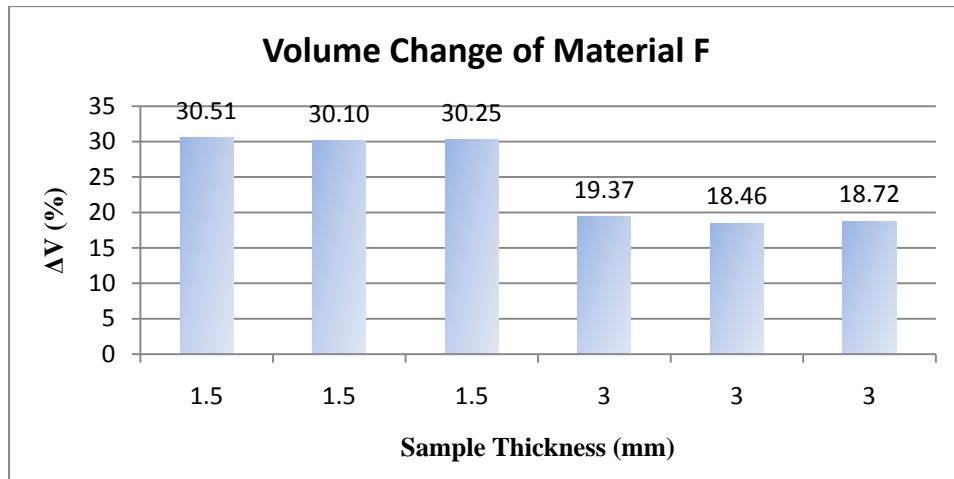


Figure 8.6. Results from immersion test of Material F from the first phase of tests. Y-axis shows the volume percentage that each sample swelled in the test and X-axis shows the thickness of the material

The average swelling of 1,5 mm thick samples was 30,29 % and for 3,0 mm thick samples, the average swelling was 18,85 %. This material will be tested in the second phase of tests, because the result for 3,0 mm thick samples are good.

In Figure 8.7 there are the average values of all the materials from 1,5 mm thick samples, standard deviations are added. All tested samples are included.

As can be seen from the results, there is only one material which is qualified according to UL 50 standard. The standard states, that maximum swelling of the material is 25 %. The only qualifying material, Material D, does not have a fire classification, so it does not meet our standards for the gasket material.

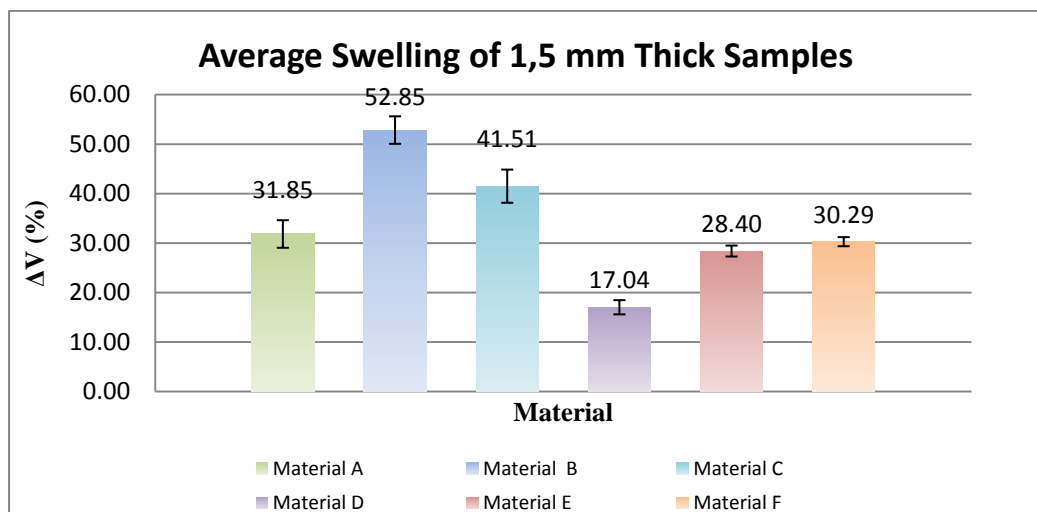


Figure 8.7. Average swelling of 1,5 mm thick samples of all materials tested. The averages are counted from all tested samples.

In Figure 8.8 there are collective results of 3,0 mm thick samples with standard deviations for each material. As can be seen from the figure, Material B is the only material which swells more than the allowed 25 %.

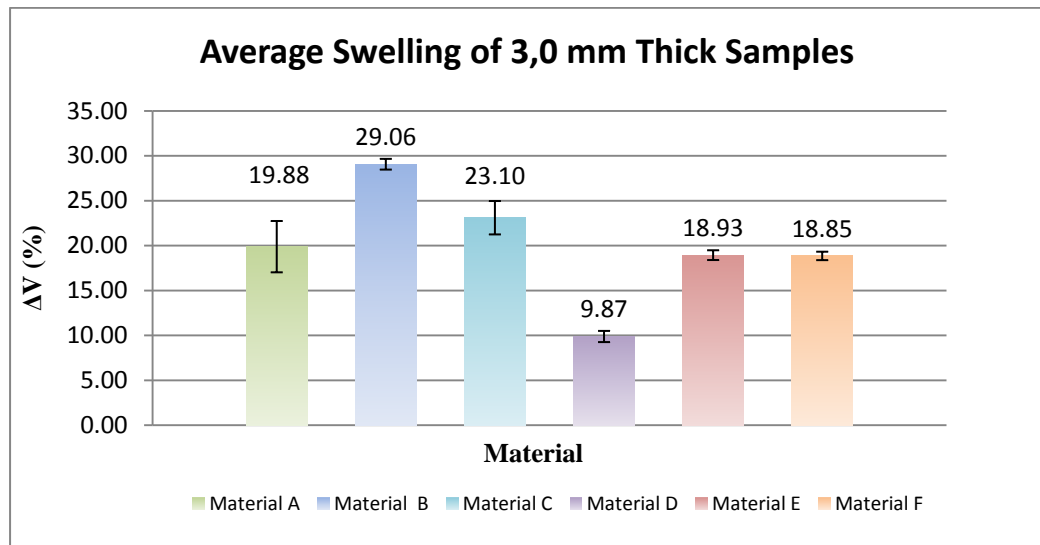


Figure 8.8. Average swelling of 3,0 mm thick samples of all materials tested. The values include the results of all tested samples.

It can be seen, that the materials act similarly regardless of the sample. For example, Material D is in both cases the one which swells the least of all the materials, just as Material B is the one which swells the most. These two specimens were quite similar, because they were the same shape but different thickness.

8.2 Immersion Test Results, Second Phase

The materials tested in the second phase were Material E, Material C Material A and Material F. Material B was excluded because of bad results from the first phase and Material D does not have fire classification, so it cannot be used in the final product.

The second phase of the tests was performed the same way as the first, with the exception of the samples' size. These samples were an inch long and wide and the thicknesses were 0,8 mm, 1,5 mm and 3,0 mm.

The first tested material was Material C. The results can be seen in Figure 8.9.

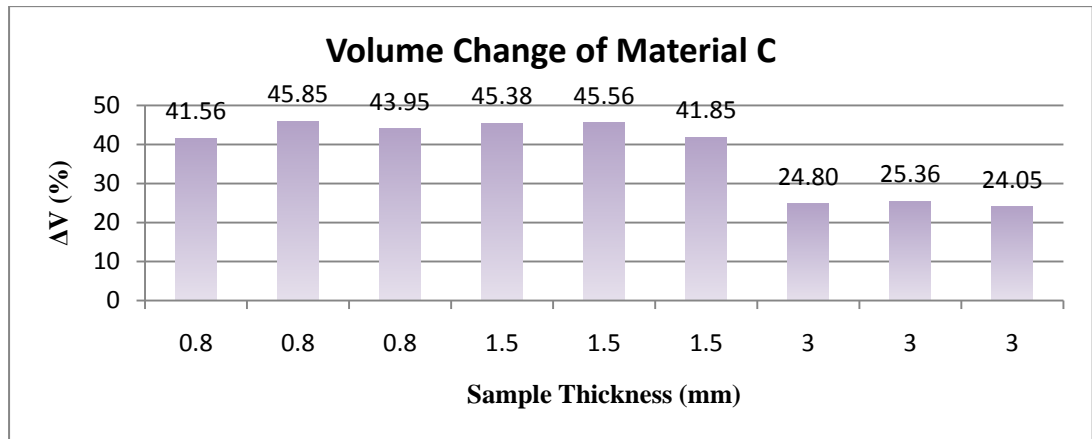


Figure 8.9. The results from the second phase of the immersion tests for Material C. Y-axis shows the change in volume in percents and X-axis shows the thickness of tested samples.

The results for 0,8 mm thick samples and 1,5 mm thick samples are unacceptable, since their average swellings were 43,79 % and 44,26 % respectively. The result for the 3,0 mm thick samples was barely acceptable with the average swelling of 24,73 %.

The second material tested was Material E, the results can be seen in Figure 8.10. The average swelling of 0,8 mm thick samples was 19,10 %. 1,5 mm thick samples was 27,94 % which is above the 25 % limit the UL 50 has set. The samples with 3,0 mm thickness had the average of 19,07 % of swelling, which is within the limit as well as the average of 0,8 mm thick samples. Two sets of samples were tested from the geometry which thickness was 0,8 mm.

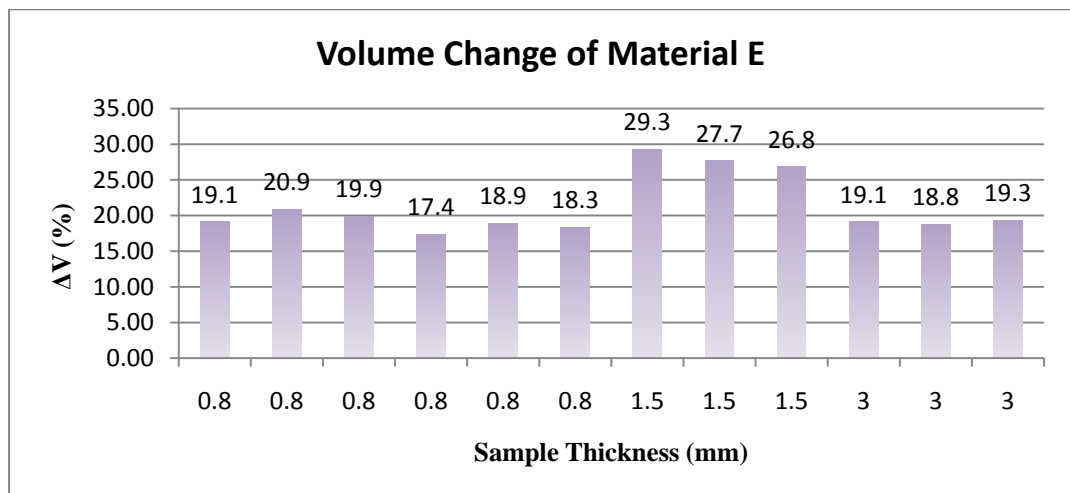


Figure 8.10. The results from the second phase of the immersion tests for Material E. Y-axis shows the change in volume in percents and X-axis shows the thickness of tested samples.

The third material tested in the second phase of tests was Material A. The results can be seen in Figure 8.11. The average of swelling of 0,8 mm thick samples was 27,93 %, 1,5 mm thick samples 33,83 % and of 3,0 mm thick samples 22,39 %. Only the 3,0 mm thick samples stay under the limit of 25 %.

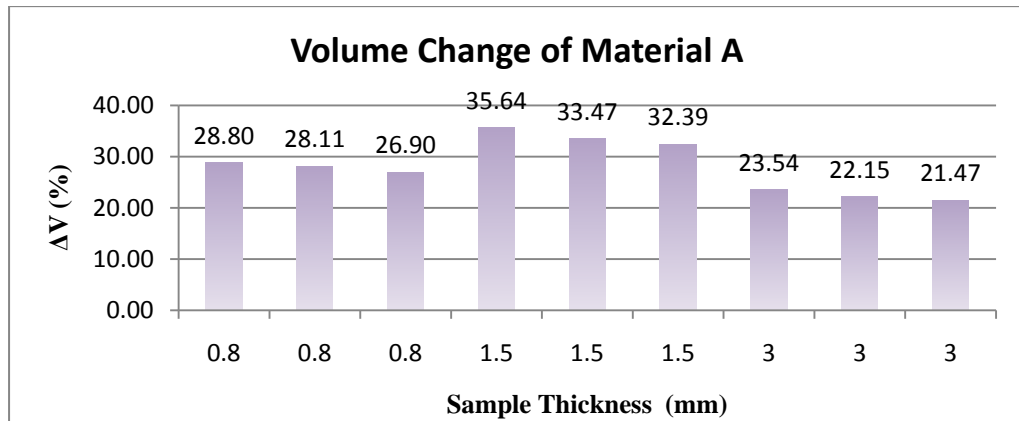


Figure 8.11. The results from the second phase of the immersion tests for Material A. Y-axis shows the change in volume in percents and X-axis shows the thickness of tested samples.

The last material tested was Material F, its results can be seen in Figure 8.12.

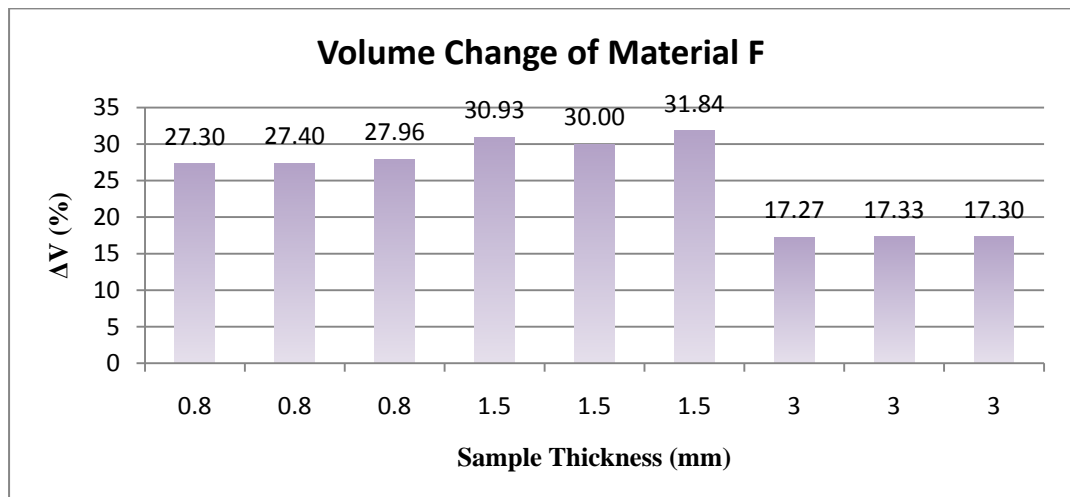


Figure 8.12. The results from the second phase of the immersion tests for Material F. Y-axis shows the change in volume in percents and X-axis shows the thickness of tested samples.

Again the only sample thickness that was acceptable was 3,0 mm thick samples with their average swelling of 17,30 %. 0,8 mm and 1,5 mm thick samples' results were 27,55 % and 30,92 % respectively.

In Figure 8.13 there is a collective review on the results of 0,8 mm thick samples for each material. Standard deviations are also marked for each material. It would appear that Material C is the weakest material of the group and Material E is the strongest. Differences in the swelling percentage between materials are quite large.

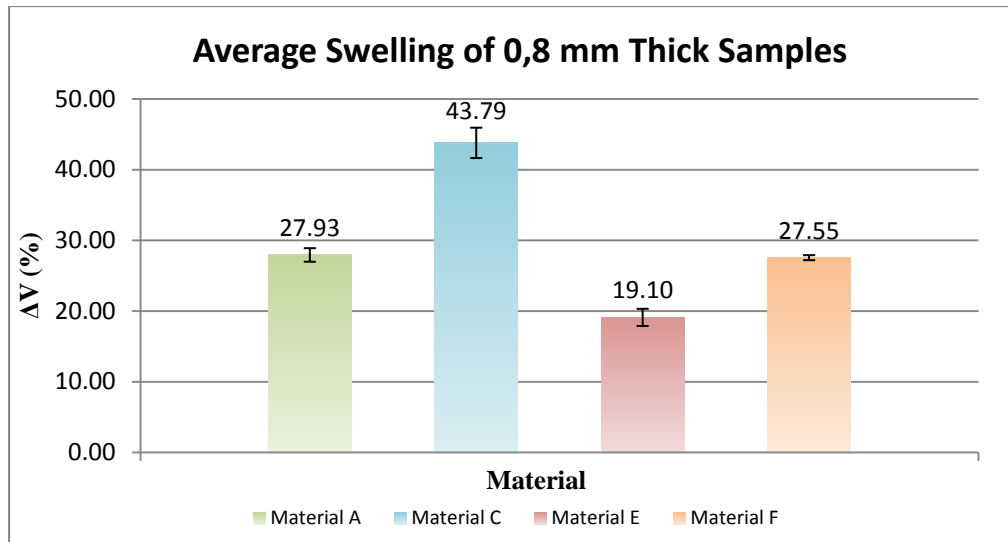


Figure 8.13 Average swelling of 0,8 mm thick square shaped samples of all materials tested. The values include the results of all samples tested.

In Figure 8.14 there is another collective review with each material's standard deviations. In this figure, there are samples which are 1,5 mm thick. Here, too Material C swells the most and Material E the least, but the differences between materials are smaller here, than in the previous Figure 8.13.

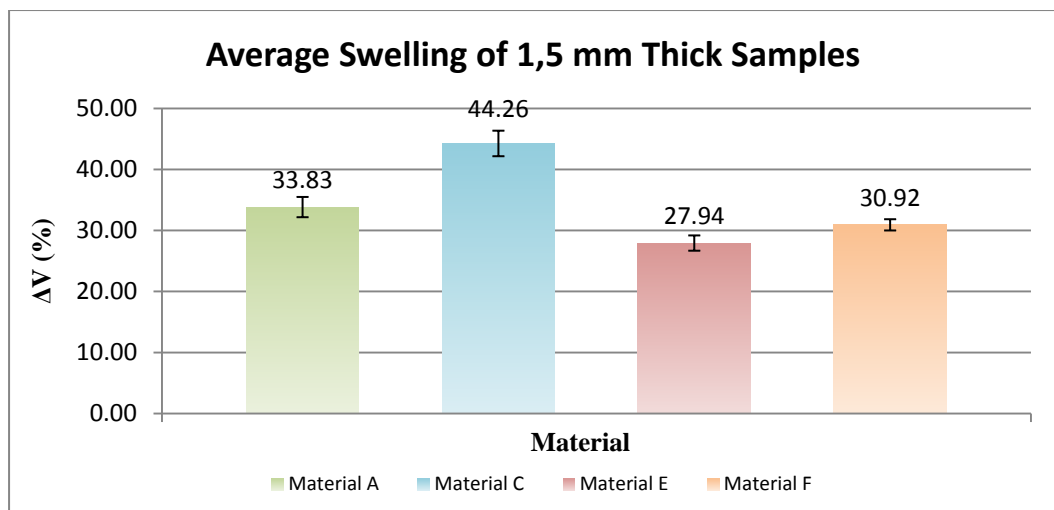


Figure 8.14 Average swelling of 1,5 mm thick square shaped samples of all materials tested. The values include the results of all tested samples.

The same kind of pattern continues in Figure 8.15, where are the collective results of 3,0 mm thick samples from the second phase with standard deviation for each material. Again, Material C swells the most but this time Material F swells the least. The differences in the swelling percent are smaller with 3,0 mm thick samples that they were with 0,8 mm and 1,5 mm thick samples.

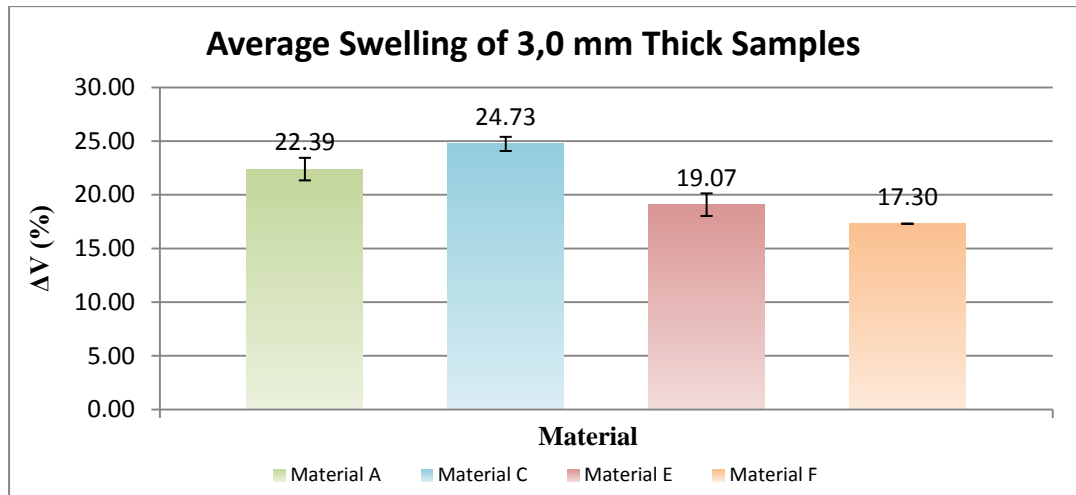


Figure 8.15. Average swelling of 1,5 mm thick square shaped samples of all materials tested. The values include the results of all tested samples.

8.3 Immersion Test Results, Third Phase

In the third phase of tests the test specimens were shaped like real products. Materials A, C and E were tested, as the specimens made of the third material (Material F) had some logistical problems and they did not arrive in time to be tested for this thesis. They will be tested later.

In Figure 8.16 there are results for Material A.

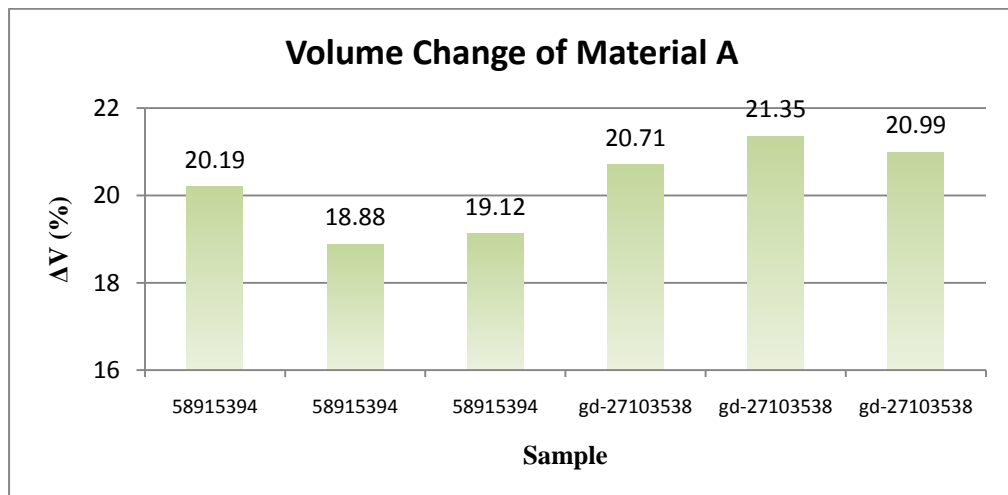


Figure 8.16. The results from the third phase of the immersion tests for Material A. Y-axis shows the change in volume in percents and X-axis shows the samples tested.

Both geometries swell less than 25 %. The average swelling for 58915394 was 19,40 % and for gd-27103538 21,01 %. The differences between parallel samples of 58915394 are quite large. In this case, the weighing of the sample was difficult, because the geometry of the sample allowed a lot of air bubbles on to the surface of the specimen and all could not be successfully removed.

Next material tested was Material C. Results from the test are in Figure 8.17. The average results for 58915394 was 22,90 % and for gd-27103538 was 22,31 %, which both are under the 25 % limit.

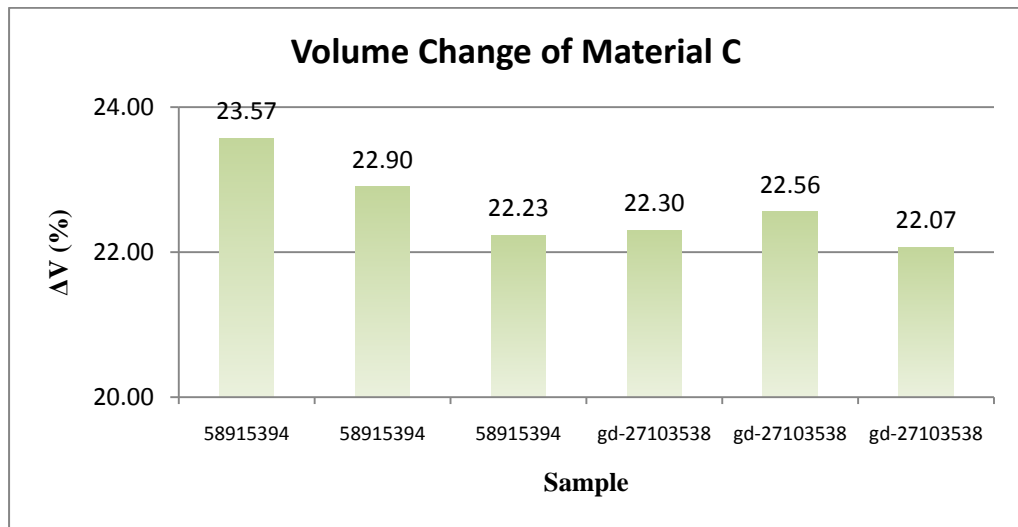


Figure 8.17. The results from the third phase of the immersion tests for Material C. Y-axis shows the change in volume in percents and X-axis shows the samples tested.

Here again was the same air bubble problem during the measurements and this is why the results of parallel samples of 58915394 are so far apart.

The last tested material in phase three was Material E. Results from that test are in Figure 8.18. The average volume change was 17,13 % for 58915394 and 18,85 % for gd-27103538.

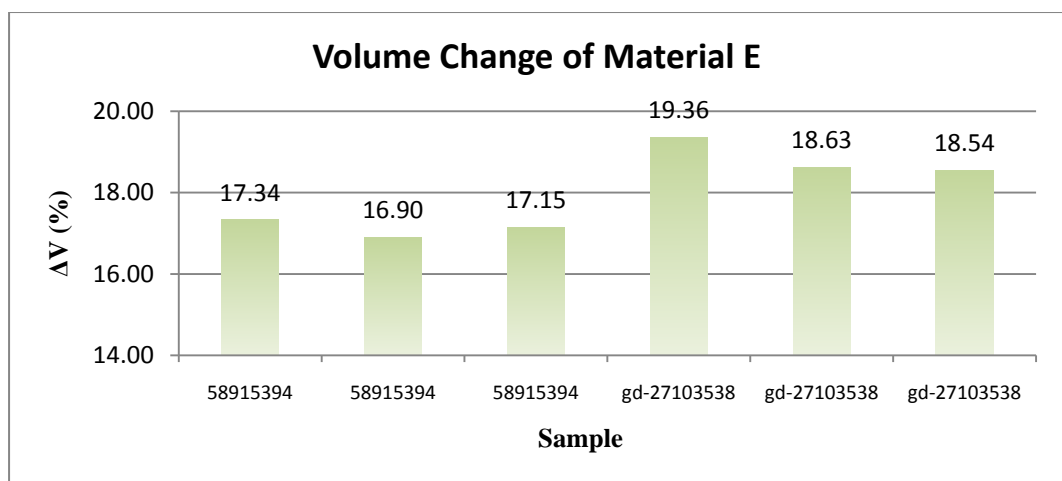


Figure 8.18. The results from the third phase of the immersion tests for Material C. Y-axis shows the change in volume in percents and X-axis shows the samples tested.

Collective review of the third phase results for 58915394 with standard deviation for each material is in Figure 8.19. Here too Material C swells the most. All these samples swelled under the limit of 25 %.

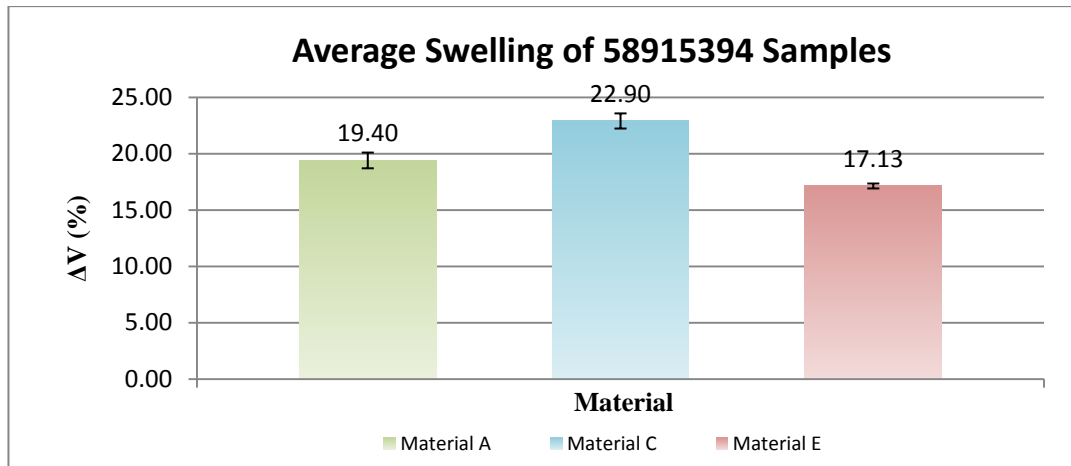


Figure 8.19. Average swelling of 58915394 samples. X-axis shows the material and Y-axis shows the swelling percent.

The same kind of results can be seen in Figure 8.20, where average results are shown for gd-27103538 with standard deviation for each material. In this figure too, Material E swells the least. Again all samples stayed under the 25 % limit.

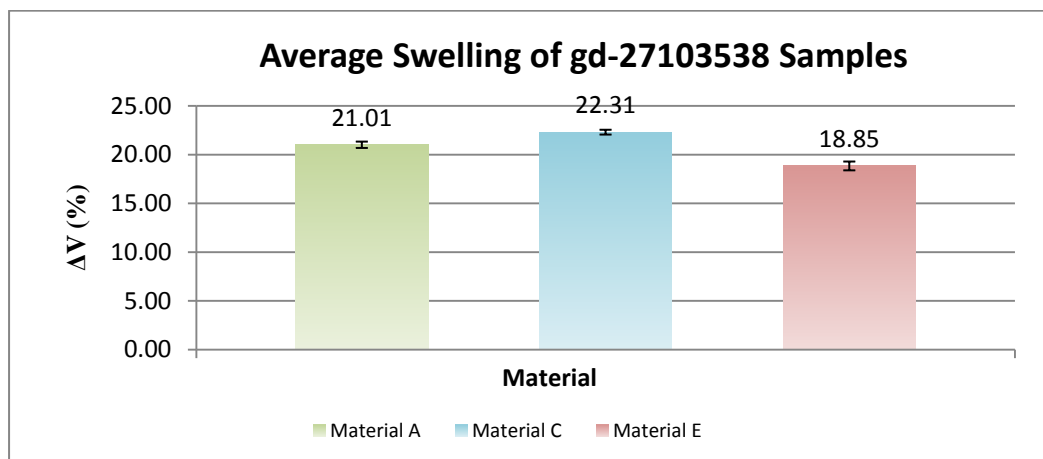


Figure 8.20. Average swelling of gd-27103538 samples. X-axis shows the material and Y-axis shows the swelling percent.

8.4 Results of the Density Measurements

Densities were measured in order to draw conclusions from the effect of density on the swelling of the samples. The results and densities given to each material by its individual data sheet can be found in Table 8.1.

Table 8.1. Results of the density measurements and densities given to each material by its individual data sheet.

Material	Measured Density (g/cm³)	Density from Data Sheet (g/cm³)
A	1.241	1.24
B	1.213	1.25
C	1.272	1.27
D	1.023	1.02
E	1.21	1.2

The measurements proved the densities to be the same as the data sheets had given to all materials except material B. The measurement was done in water, so it is possible that the results were distracted by air bubbles which formed on the surface of the materials even though they were very carefully removed. In the results analysis section of this thesis, the effect of density on swelling is considered.

8.5 Error Evaluation

As can be seen from the results of the immersion tests, the tested specimens swelled different amounts between parallel samples. This is odd considering, that all parallel samples were made from the same material in the same geometry. Here is some consideration why errors occur.

The immersion tests were done by hand with equipments which were not especially designed for this purpose. This may cause error to the results. For example, when the samples were wiped after they were taken out of the oil, the amount of oil removed by wiping makes the sample lose weight. The amount of oil removed from the surface of the sample could not be standardized, so the amount had to be assessed by eye. This lead to a situation where different amount of oil was removed from every samples surface.

Another situation where error could have happened was the weighing of the sample in water. When lowered in water, some air bubbles were always left on the surface of the samples. The bubbles were obviously removed as accurately as possible, but it is possible that some bubbles remained in the surface of the sample, this skewing the weight.

The samples tested were not all exactly the same shape and size. In some samples the injection point was receded a bit, so the volume and area of the samples may have varied.

9 RESULT ANALYSIS

A part of this thesis was to find out, which variables in the geometry of the material affect swelling. First, it was considered, if there was a dependency between the swelling and volume or area of the samples. Then swelling's dependency on volume/area ratio was considered. Also, density's affect on swelling was pondered.

9.1 Effect of Area on Swelling

The dependency between swelling and area is presented in Figure 9.1. Area is located on X-axis and change of volume percentage is on Y-axis. The average a value of each sample's swelling was used in this graph.

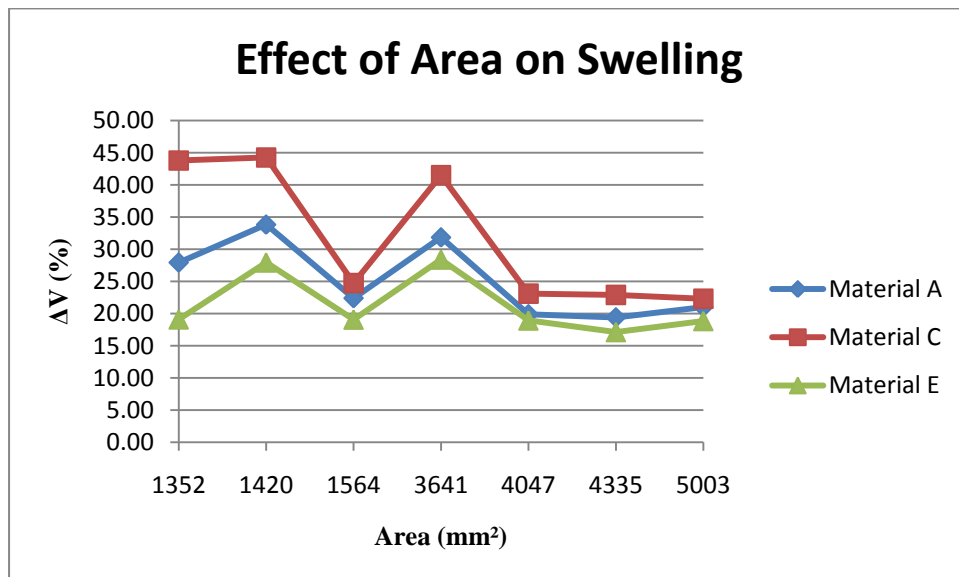


Figure 9.1. The dependency between swelling and area. X-axis shows area and Y-axis shows the change of volume percentage.

It would seem that there is no clear dependency between area and swelling percentage though all materials act quite similarly. This is may be due to other reasons, because based on this graphic it seems impossible to predict how other samples made from these materials will swell if their area is known.

9.2 Effect of Volume on Swelling

The dependency between swelling and area is presented in Figure 9.2. Volume is located on X-axis and change of volume percentage is on Y-axis. The average a value of each sample's swelling was used in this graph.

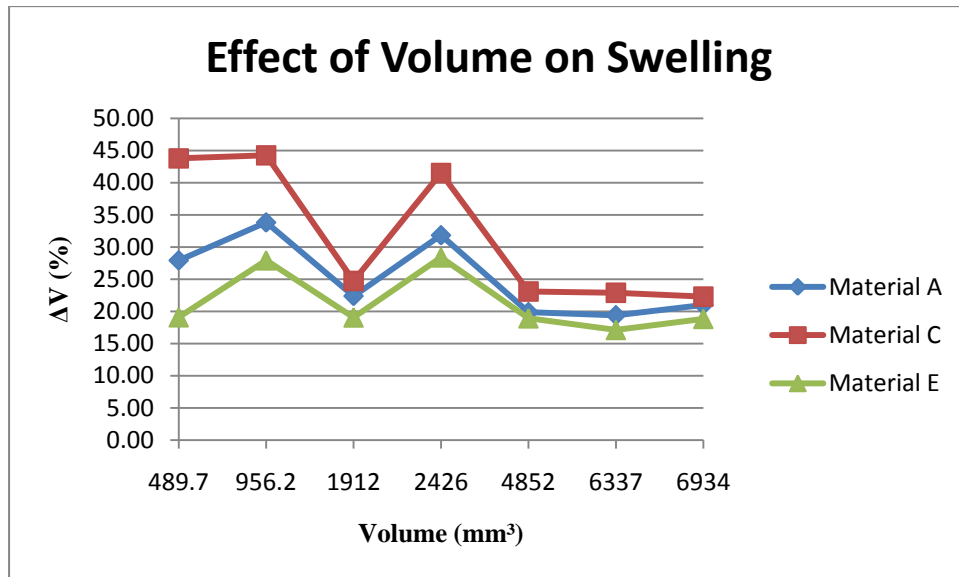


Figure 9.2 The dependency between swelling and volume. X-axis shows volume and Y-axis shows the change of volume percentage.

No clear dependency is visible here either. Again all materials seem to be acting similarly, but since no clear dependency by which the swelling could be predicted does exist, the similar behavior must be due to other reasons.

9.3 The Dependence between Volume/ Area Ratio and Swelling

This section shows the dependence of the volume/area ratio on swelling of materials and forms a pattern between the ratio of volume/area and swelling, so that if the V/A ratio is known, the swelling percentage can be predicted. The figures have been drawn only for materials which have been tested in more geometries than two, this being only those materials which were tested in phase two and/or three.

9.3.1 Material A

Figure 9.3 shows the swelling of each sample and its V/A ratio. The figure also shows the average swelling of each sample form. The red line in the figure shows the 25 % line, under which the samples are qualified by the UL standard.

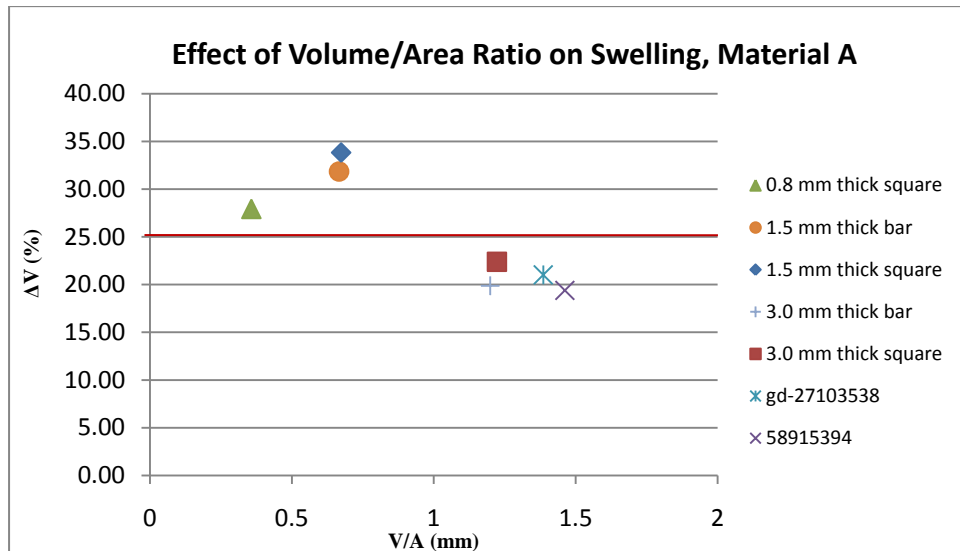


Figure 9.3. The effect of volume/area ratio on swelling for Material A. In the X-axis there are the V/A ratio of the samples. Y-axis shows the change in volume caused by the swelling in the sample. Samples under the red line are accepted by the UL standard.

It can be seen from this figure that the samples which were in the form of real gaskets are under the UL standard set limit. This should be the case, because this material is used in real products at the moment.

It can also be noted, that if the V/A ratio is over one, the material is likely to swell less than 25 %. In the smaller ratios, the swelling seems to be greater.

In theory, all the marks with same V/A ratio should be in one place. This isn't the case in this figure, for example the averages of 1,5 mm thick bar and 1,5 mm thick square should be closer together, as well as 3,0 mm thick bar and 3,0 mm thick square. It must be remembered, that the measurements were done by hand and thus there are some inaccuracies compared to measurements done by machines or theory.

In Figure 9.4 there is a linear trendline fitted to the dots seen in Figure 9.3. The idea was to see, if the swelling of a sample with a known V/A ratio could be determined using the line.

The marks do not fit the line perfectly, but some predictability can be seen. The mark which represents 0,8 mm thick square sample average is much lower than would be expected, if the swelling of the sample should be predicted from the trendline. One reason for this may be that it has reached its saturation point, that it cannot contain more oil than it does in this case. If this was true though, the mark should be discarded from the formation of the trendline, since it skews this line. If this was done, the trendline would be a better fit. Since this has not been investigated during this thesis, it cannot be discarded.

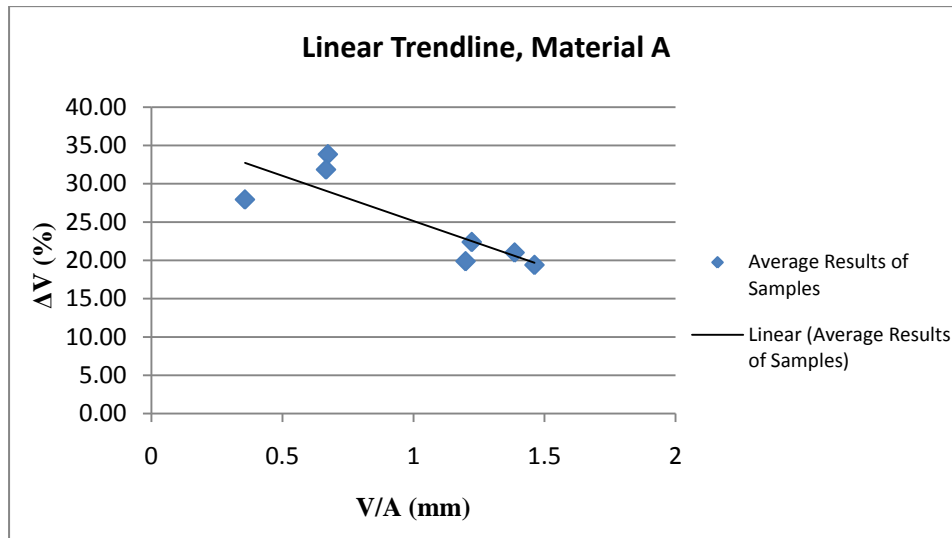


Figure 9.4. Trendline fitting for Material A. Explanation for marks can be seen in figure 9.3.

9.3.2 Material C

Figure 9.5 shows the average swelling of each sample and its V/A ratio. The figure also shows the swelling of each sample form. The red line in the figure shows the 25 % line, under which the samples are qualified by the UL standard.

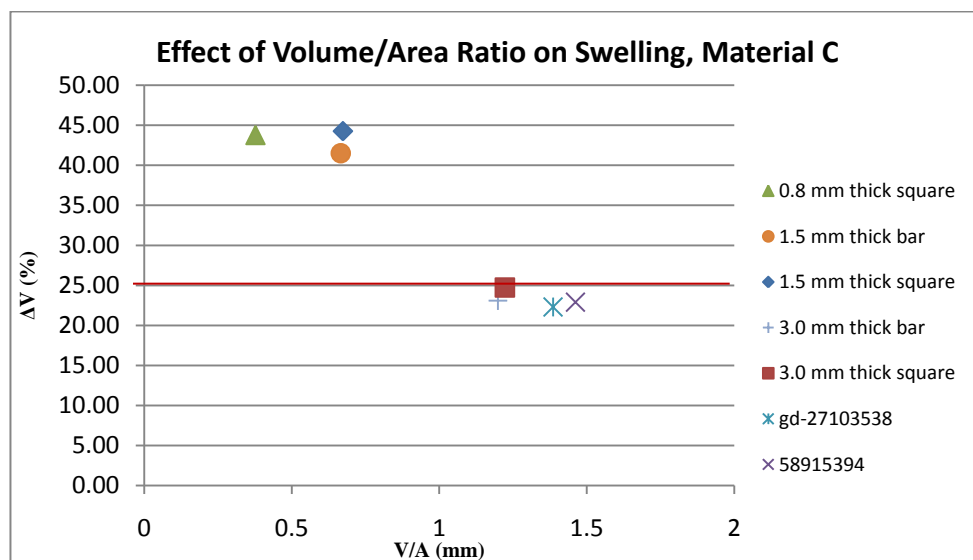


Figure 9.5. The effect of volume/area ratio on swelling for Material C. In the X-axis there are the V/A ratios of the samples. Y-axis shows the change in volume caused by the swelling in the sample. Samples under the red line are accepted by the UL standard.

The 1,5 mm thick samples should be closer together as should the 3,0 mm thick samples. It would be assumed, that the average of 0,8 mm thick samples should be gra-

ter, but again as in the case of Material A it might be because it has reached its saturation point.

Only the real gasket forms qualified in these tests. The samples with V/A ratio of 1.2 are on the line, and if forms with this V/A ratio are used, new tests are necessary.

In Figure 9.6, there is a trendline fitting done to the marks in the previous Figure 9.5. The marks do not fit the line perfectly, but approximations can be made quite reliably.

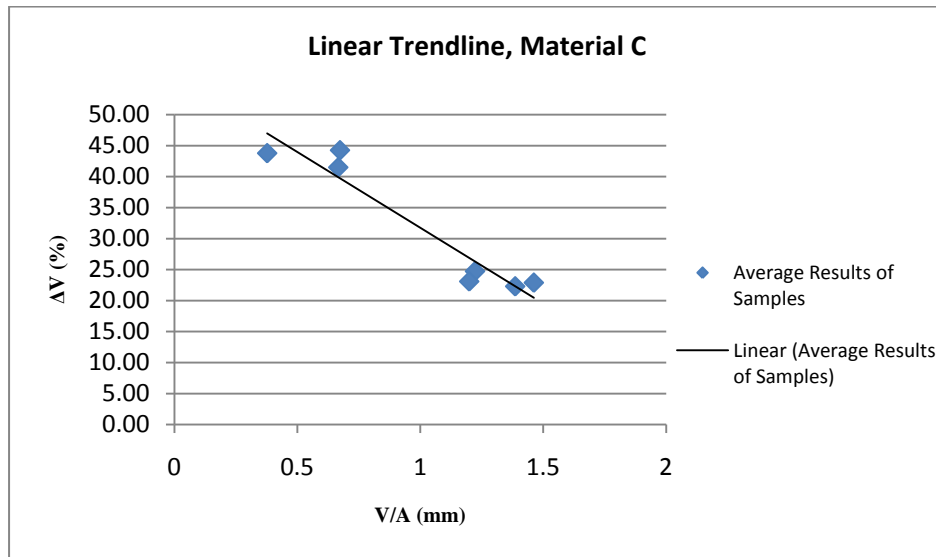


Figure 9.6. Trendline fitting for Material C. Explanation for marks can be seen in figure 9.5.

9.3.3 Material E

Figure 9.7 shows the average swelling of each sample and its V/A ratio. The figure also shows the swelling of each sample form. The red line in the figure shows the 25 % line, under which the samples are qualified by the UL standard.

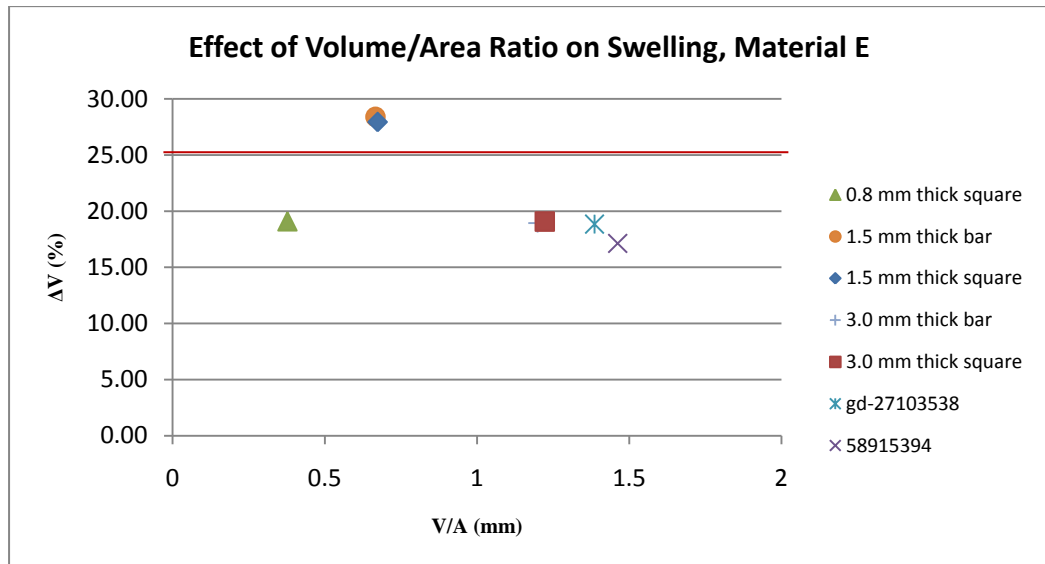


Figure 9.7 The effect of volume/area ratio on swelling for Material E. In the X-axis there are the V/A ratios of the samples. Y-axis shows the change in volume caused by the swelling in the sample. Samples under the red line are accepted by the UL standard.

In the figure above, the 1,5 mm thick samples and the 3,0 mm thick samples are in the same place as they should be according to theory. This material is the most oil resistant of all materials tested in this thesis, because the 3,0 mm thick samples , gd-27103538 samples and 58915394 samples are under the 25 % limit.

A linear trendline fitting was done to Material E also. Result is in Figure 9.8.

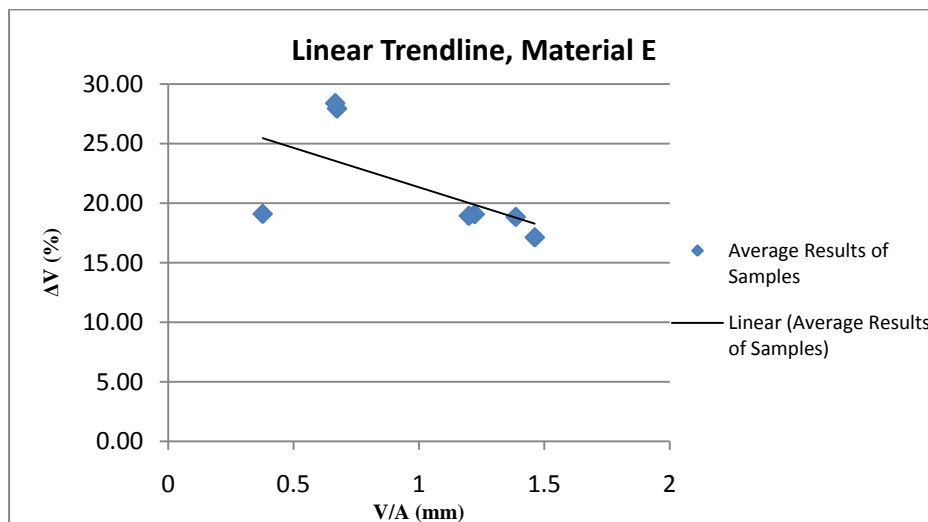


Figure 9.8 Trendline fitting for Material A. Explanation for marks can be seen in figure 9.7.

It seems that the other marks are well in line with each other, but the 0,8 mm thick samples' mark is skewing the figure. Because of this, a test was done to 0,8 mm thick samples made from Material E to determine if the samples have reach their satiation point in 70 hours. The swelling was measured in certain time intervals. Results are in Figure 9.9.

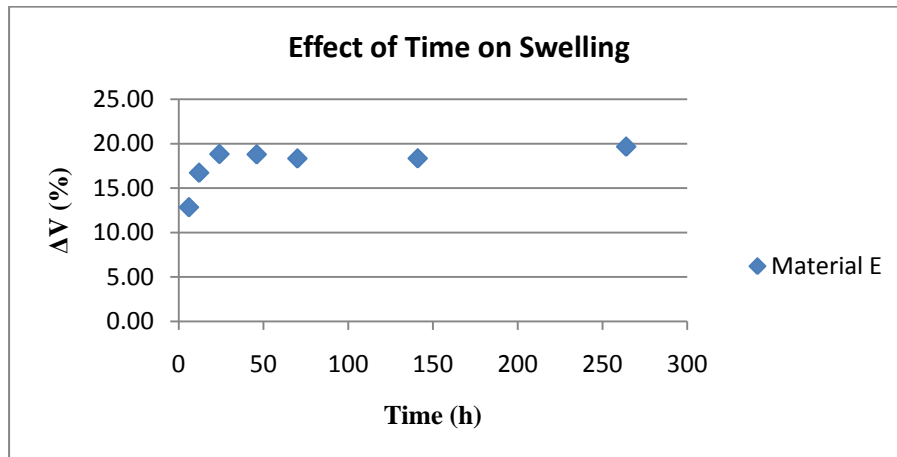


Figure 9.9. The effect of time on swelling was tested on 0,8 mm thick square shaped specimens made from Material E.

It seems, that indeed, the samples have reached their saturation point and that they do not swell more than maximum of 20 %. The measurements were done on separate samples so the pattern in the figure sways a bit.

If the results from the time test are taken in to account, the trendline for Material E looks like in Figure 9.10.

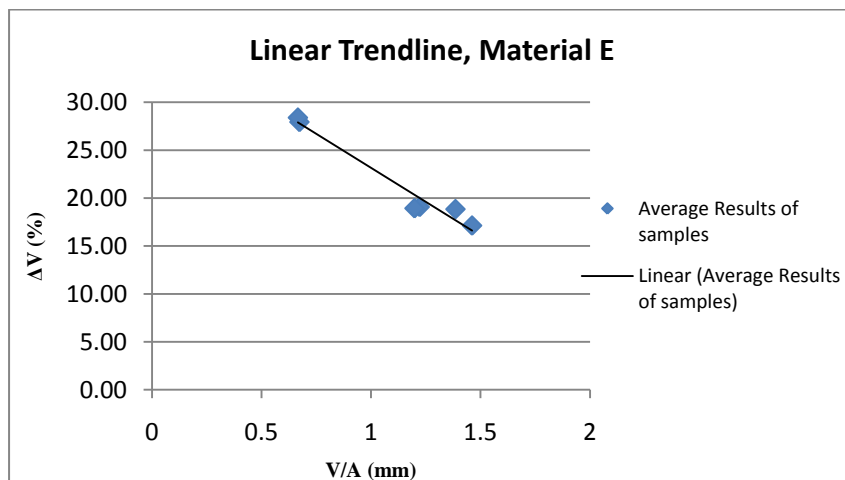


Figure 9.10. Linear trendline for Material E without 0,8 mm thick samples.

This new linear trendline can be used to predict more accurately the swelling of a sample which V/A ratio is known.

9.3.4 Material F

Figure 9.11 shows the average swelling of each sample and its V/A ratio. The figure also shows the swelling of each sample form. The red line in the figure shows the 25 % line, under which the samples are qualified by the UL standard.

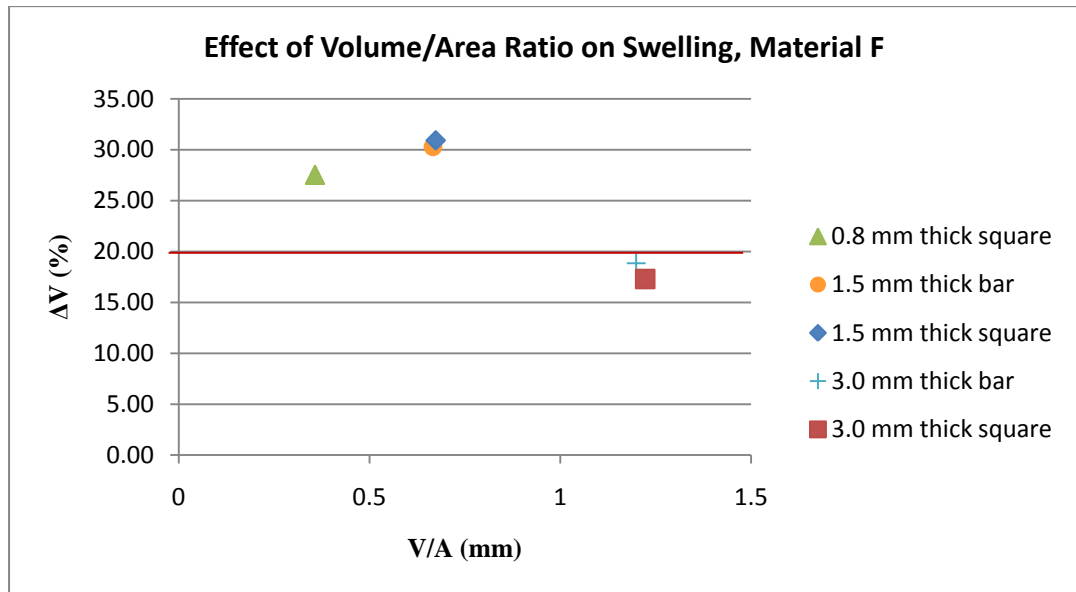


Figure 9.11. The effect of volume/area ratio on swelling for Material F. In the X-axis there are the V/A ratios of the samples. Y-axis shows the change in volume caused by the swelling in the sample. Samples under the red line are accepted by the UL standard.

In the case of Material F the third phase tests were left out. There are only five test geometries. The 1,5 mm thick samples are well in the same place but the 3,0 mm thick samples are a bit apart. Again the 0,8 mm sample is lower than expected, but because time test was not done on this material that mark cannot be excluded from the trendline fitting (Figure 9.12). Since there aren't many marks in the graph for Material F the linear trendline is not as reliable as for the other materials.

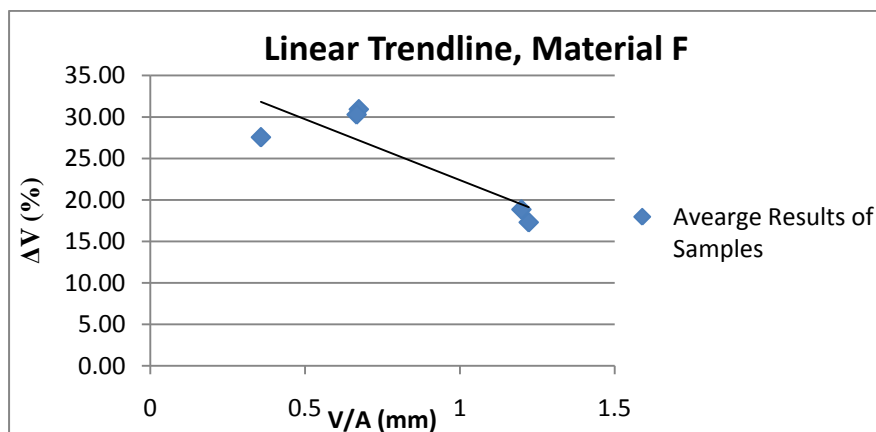


Figure 9.12. Trendline fitting for Material F. Explanation for marks can be seen in figure 9.11

9.4 The Effect of Density on Swelling

The effect of density on swelling is shown in Figure 9.13. Average swelling results for each sample and material were used in this graph as well as measured densities.

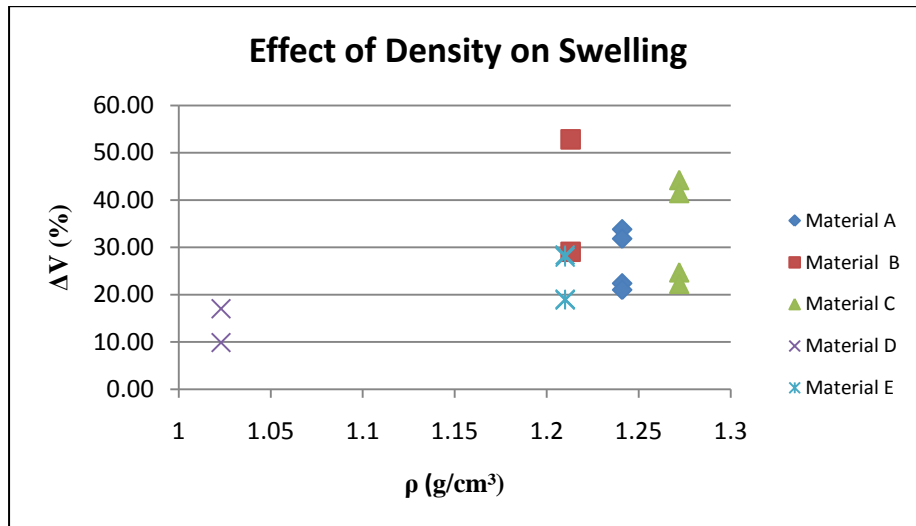


Figure 9.13. The effect of density on swelling. Graph is made using average swelling results from each sample geometry and material. Densities used here were measured.

Based on the figure above, the densities do not seem to have a clear effect on swelling, or at least the marks on the graph don't form a pattern from which the amount of swelling could be determined if swelling is known.

10 CONCLUSIONS

From theoretical point of view, the best material group to find a material for this kind of purpose is TPU, since it has so wide range of properties depending of its structure. Co-polyester based elastomers would also be a good group to search for a suitable material if a bit harder materials would be allowed.

One factor helping to predict swelling is solubility parameter. The closer solubility parameters of oil and elastomer are to each other, the more the material will swell due to that oil. Solubility parameters are usually the same scale with materials and oils which have the same kind of structure. For example hydro-carbon elastomers swell by hydro-carbon solvents, but not by polar solvents.

According to the tests, the most suitable gasket material, taking into account all requirements, is Material E. It is made of SEBS which has good chemical resistance properties, wide range in hardness and good tear strength. Material E has an acceptable hardness and tear strength. Also it was the material which swelled the least in all the tests. This material's swelling behavior can be predicted quite well based on the V/A ratio.

Other suitable material is Material C, especially if the gaskets made from this material have V/A ratio over 1,2. Material F seems to be promising too, but it requires some additional tests to confirm its properties.

The only geometrical factor found to contribute materials swelling was V/A ratio. Once the graph is made for a certain material, it helps to predict the swelling of a sample with a certain V/A ratio made from the same material.

The tests made for this thesis will continue after this thesis is completed. Some new sample geometries and new materials will be tested.

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