



TAMPERE UNIVERSITY OF TECHNOLOGY

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FOAMING OF THERMOPLASTIC ELASTOMERS
Master of Science Thesis

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ABSTRACT

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The objective of this Master of Science thesis was to find out whether foaming could be implemented to offer new property-combinations for gaskets in electrical devices. Gaskets used as a basis of the study are made of solid thermoplastic elastomers. Low hardness and compression set combined with high resistance to fire and oil are required. Achieving these properties with blending has proven to be difficult, and foaming as a solution is studied.

The thesis consists of a theoretical and an experimental part. In the theoretical part structure and classification of thermoplastic elastomers, fundamentals and methods of foaming as well as related rheology are discussed. Previous studies done on the subject are also reviewed. In the experimental part two thermoplastic elastomer materials were foamed and effects on properties were observed. Also a rheological characterization of the materials was done.

Thermoplastic elastomers combine mechanical properties of elastomers and easy processing of thermoplastics. Those properties are usually achieved in polymer blends or copolymers. Foaming means introducing gas filled cells into the material. Viable foaming methods for gasket materials are physical, chemical and syntactic foaming. In syntactic foaming gas filled glass or polymer spheres are added to a material. Hydrocarbon filled polymer spheres expand during processing, creating thin walled cells. These spheres are called expandable microspheres.

In the experimental part two styrenic thermoplastic elastomers were foamed using expandable microspheres. Achieved cell structures were heterogeneous as density expectedly varied throughout the part. Hardness decreased with density, but also a hardening effect of microspheres was seen. A similar density dependency was seen in compression deflection. Compression set on the other hand increased noticeably for all foams, but no dependency to density or cell size was noticed. Flammability increased expectedly but oil swell decreased which was not expected. More oil had permeated foams than solids, but cells rather than polymer structure were filled, keeping the swelling moderate. Behaviour of the materials in shear and extensional deformation was evaluated in rheological characterization. Materials had noticeable differences and it could be deduced that one would be more suitable for syntactic and the other for physical and chemical foaming.

From the experimental part it can be concluded that foaming is indeed a possible way of improving gasket materials. Results of this work have been promising, but more research needs to be done on the subject.

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Tämän diplomityön tavoitteena oli selvittää, voisiko solustuksella tuoda uusia ominaisuusyhdistelmiä sähkölaitteiden tiivisteiden materiaaleihin. Tiivisteet joihin työ pohjautuu, valmistetaan solustamattomista termoplastisista elastomeereistä, joilta vaaditaan alhaista kovuutta ja jäännöspuristumaa yhdistettynä hyvään öljyn ja tulen kestävyYTEEN. Koska tarvittavien ominaisuuksien saavuttaminen seostamisella on osoittautunut hankalaksi, haetaan ratkaisua solustamisesta.

Työ koostuu teoreettisesta ja kokeellisesta osasta. Teoreettisessa osassa käsitellään termoplastisten elastomeerien rakenne ja luokittelu, solustuksen perusteet, menetelmät ja siihen liittyvä reologia, sekä tehdään yhteenveto aiheen aikaisemmista tutkimustuloksista. Kokeellisessa osuudessa kahta termoplastista elastomeeriä solustettiin ja vaikutusta ominaisuuksiin tarkkailtiin. Materiaaleille tehtiin myös reologinen analyysi.

Termoplastiset elastomeerit tuovat yhteen elastomeerien mekaaniset ominaisuudet ja kestonmuovien helpon prosessoitavuuden. Materiaalien ominaisuudet saavutetaan yleensä joko seostamalla tai kopolymeereillä. Solustus puolestaan tarkoittaa kaasua sisältävien solujen tuomista materiaaliin. Mahdollisia menetelmiä tiivisteille ovat fysikaalinen, kemiallinen ja syntaktinen solustus. Syntaktisessa solustuksessa materiaaliin tuodaan kaasua sisältäviä lasi- tai polymeeripalloja. Hiilivetyä sisältävät polymeeripallot laajenevat prosessoinnin aikana, muodostaen ohutseinämäisiä soluja. Niitä kutsutaankin laajeneviksi mikropalloiksi.

Kokeellisessa osuudessa kahta styreenipohjaista termoplastista elastomeeriä solustettiin käyttämällä laajenevia mikropalloja. Saadut solurakenteet olivat heterogeenisiä, sillä materiaalin tiheys muuttui odotetusti läpi kappaleen. Kovuus laski tiheyden mukaan, mutta mikropallojen kovuutta lisäävä vaikutus oli nähtävissä. Myös puristuspoikkeuma osoitti selvää tiheysriippuvuutta. Jäännöspuristuma nousi kaikilla solumateriaaleilla, mutta yhteyttä tiheyteen tai solukokoon ei havaittu. Palon kesto heikkeni solustettaessa odotetusti, mutta öljyturpoama odottamatta laski. Öljyä imeytyi solustettuihin kappaleisiin huomattavasti enemmän kuin solustamattomiin, mutta turpoama pysyi kohutuullisena, sillä polymeerirakenteen sijasta täyttyivät solut. Reologisessa analyysissä materiaalien leikkaus- ja venymäkäyttäytymistä arvioitiin. Materiaalit erosivat toisistaan selvästi, ja voitiin päätellä toisen soveltuvan paremmin syntaktiseen, ja toisen kemialliseen ja fysikaaliseen solustukseen.

Kokeellisen osuuden yhteenvetona voidaan todeta, että solustaminen on mahdollinen tapa kehittää tiivistemateriaaleja. Työn tulokset ovat lupaavia, mutta lisätutkimusta aiheesta kaivataan.

PREFACE

This Master of Science thesis was funded with a grant from The Industrial Research Fund at Tampere University of Technology. The scope was to find out how foaming affected properties of thermoplastic elastomers.

While writing I got to explore not only the world of foaming, but also thermoplastic elastomers, rheology and expandable microspheres. I was lucky to get the chance to travel to Sweden and meet with the people of Expancel.

Because the thesis combines so many fields of expertise, I have a long list of people to thank. First I would like to thank my supervisor professor Pentti Järvelä, not only for the instruction and advice during the thesis, but also for the educational work assignments he has given me during my time as a part-time worker at The Laboratory of Plastics and Elastomer Technology. I would also like to thank Vesa Palojoiki, electrical device expert for the thesis, from ABB Ltd. Drives for the knowledge and help I received, as well as for organizing the trip to Sweden. Also Pekka Uskali from Trelleborg deserves to be thanked since he has taken part in meetings and decision making from the start and supplied the reference samples.

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Last but not least I would like to thank my family and friends for their support and for making the last few years the best years of my life. My sister introduced me to the world of materials and my parents have supported me throughout my studies and given me inspiration to educate myself. I would especially like to thank my husband, Timo, for all his support and for letting me live of him during my studying years.

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ABBREVIATIONS AND NOTATION

$\dot{\gamma}^*$	Schümmmer corrected shear rate
$\dot{\gamma}_{wa}$	Apparent shear rate
$\dot{\epsilon}$	Extension rate
Δp	Pressure drop across capillary
Δp_e	Entrance pressure drop
D	Diameter of capillary
L	Length of capillary
n	Power-law index
Q	Volume flow rate
R	Capillary radius
R_p	Cylinder radius
v_p	Piston speed
x^*	Factor for Schümmmer approximation
η_a	Apparent shear viscosity
η_e	Extensional viscosity
σ	Tension stress
τ_w	True wall shear stress
τ_{wa}	Apparent wall shear stress
ADC	Azodicarboamide
BA	Blowing agent
B-PP	Branched polypropylene
B-TPO	Branched olefinic thermoplastic elastomer
CaCO₃	Calcium carbonate
CBA	Chemical blowing agent
CFC	Chlorofluorocarbon
CO₂	Carbon dioxide
EOC	Ethylene-octene copolymer
EP	Ethylene-propylene copolymer
EPDM	Ethylene-propylene-diene monomer
EVA	Ethylene-vinyl acetate
HCFC	Hydrochlorofluorocarbon
IIR	Isobutylene-isoprene
IRM 903	ASTM reference oil, required in standard UL 157 for oil swell testing
L-PP	Linear polypropylene
L-TPO	Linear olefinic thermoplastic elastomer
MatA	Material A, used in testing
MatB	Material B, used in testing
N₂	Nitrogen
NBR	Nitrile rubber
PAN	Polyacrylonitrile

PBA	Physical blowing agent
PE	Polyethylene
PE-HD	High-density polyethylene
PE-LD	Low-density polyethylene
PE-LLD	Linear low-density polyethylene
PET	Polyethylene terephthalate
PMAN	Polymethacrylonitrile
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SBS	Styrene-butadiene-styrene
SCF	Supercritical fluid
SEBS	Styrene-ethylene-butylene-styrene
SEM	Scanning electron microscope
SIS	Styrene-isoprene-styrene
T_g	Glass transition temperature
T_m	Crystalline melting temperature
TPC	Copolyester thermoplastic elastomer
TPE	Thermoplastic elastomer
TPO	Olefinic thermoplastic elastomer
TPS	Styrenic thermoplastic elastomer
TPU	Urethane thermoplastic elastomer
TPV	Thermoplastic (rubber) vulcanizate

1 INTRODUCTION

Thermoplastic elastomers are unique materials with a wide range of properties, filling the gap between thermoplastics and elastomers. They combine the properties of elastomers with easy processability of thermoplastics. When used to replace thermoplastics, they offer better impact resistance, which is why they are often used in car industry. When replacing elastomers they give the material easy processing, shorter cycle times and recyclability, making them a viable alternative in many applications.

Foaming is a method of introducing gas filled cells into the material. It decreases density of the product lowering weight and material cost, but at the same time affecting other properties. Combining foaming and thermoplastic elastomers offers a wide variety of possibilities to new and existing applications. Unfortunately bringing the two together is not that easy, as thermoplastic elastomers have complex structures and factors affecting foaming are not completely understood.

This Master of Science thesis was done to improve gaskets used in electrical devices. These gaskets in can be subjected to heat, oil, chemicals and even fire, which is why the requirements for gasket materials are high and often hard to meet. In order for the material to function well as a gasket and for the electrical device casing to get the desired product rating the gasket material needs to have low hardness, low compression set, high resistance to oil and low flammability. However combining these has proved to be difficult as they seem to be dependent: as hardness decreases, oil resistance decreases as well, creating a base for this thesis: How to decrease hardness without affecting properties?

The scope of this work is to find out if foaming is a practicable way of decreasing the hardness of thermoplastic elastomers without affecting its oil resistance, flammability, and compression set. In order to get a good understanding on the subject, a basic knowledge of thermoplastic elastomers and foaming need to be achieved: What are the factors that attribute to foaming? Which thermoplastic elastomers have been foamed? Which foaming methods are most suitable for them? These questions are answered in the literature part.

In the literature part first, in Chapter 2, basics of thermoplastic elastomers are discussed. The main focus is on the structure and classification. Next, in Chapters 3 and 4, foaming is introduced. Structure, categorization, effect on properties, and foaming methods are gone through. In Chapter 5 rheology of foaming is discussed. First fundamentals of rheology are revised, after which effects of foaming on rheological properties and effects of rheological properties on foaming are discussed. Last, in Chapter 6 thermoplastic elastomer foaming studies are reviewed. The reference material used in the literature part was versatile consisting of journal articles, conference proceedings,

doctoral dissertations, books and a webinar. There has also been two theses done related to the subject: Oil Induced Swelling in Thermoelastic Materials by Susanna Miettinen and Microfoaming of Engineering Thermoplastics by Jenni Ahola, which were used as a basis on the study.

In the experimental part two thermoplastic elastomers are foamed with expandable microspheres. The materials and microspheres are introduced in Chapter 7. Rheological characterization was done to the solid materials and the method and results are gone through in Chapter 8. In Chapter 9 methods and results of mechanical testing are discussed. Testing done to the materials contain density, hardness, tensile, compression, flammability and oil testing. Conclusions are found in Chapter 10, where also recommendations for the future are given.

2 THERMOPLASTIC ELASTOMERS

Elastomers are an irreplaceable group of materials. They have unique properties which enable a wide variety of applications. Unfortunately in order to attain these properties elastomers need to be vulcanized, which extends the cycle time and makes it impossible for the material to be reprocessed as such. This is why in some applications elastomers have been replaced by thermoplastic elastomers (TPE), which are a group of polymers that have the mechanical properties of elastomers and processability of thermoplastics. In addition to the aid in processing TPEs bring, there is an environmental aspect to take into account. Elastomers may be recycled and used for example as ground fillers or blast shelters in blasting sites but TPEs can be reused thermally as such by reheating and remoulding.

2.1 Structure

Elastomeric properties are given to a polymer by long chains which move easily allowing the material to deform. If the material only consists of this kind of structure the deformation is plastic and therefore non-reversible. The elastic, meaning reversible, properties are given to a material by linking the chains together. With elastomers this is done by vulcanization which forms bridges between chains, but in TPE the linking is usually done by adding hard segments to the structure, creating a two-phase system. These segments are thermoplastic which can be remoulded in high temperatures. Hard segments can be added to the molecular chain by making the material as copolymer or as independent molecules while blending. In polymer blends elastomer particles are usually dispersed in a continuous plastic phase. The difference in structures of polymer blends and copolymers is shown in Figure 2.1. Phases formed in polymer blends are in bigger scale than in copolymers where segments occur inside a molecule. There are only two TPE groups which do not have a two-phase structure: melt processable rubbers and ionomer based TPEs. Neither will be covered in this thesis. [1, 2]

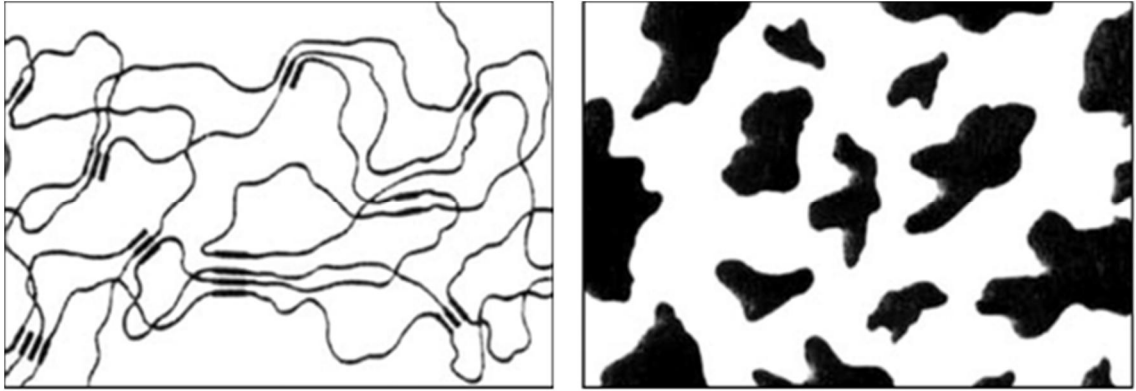


Figure 2.1. The structures of block copolymers (SBS, left) and polymer blends (right) [3].

Service temperature of a material which consists of two phases is determined by glass transition temperature (T_g) and crystalline melting temperature (T_m) of the two phases. Under T_g of both phases the material is hard and brittle. As temperature rises over T_g of the soft phase material gains its elastic properties. If temperature is raised above T_m of the hard plastic phase material melts and can be re-shaped. Flexural modulus of soft and hard thermoplastic elastomers as a function of temperature is represented in Figure 2.2. [1]

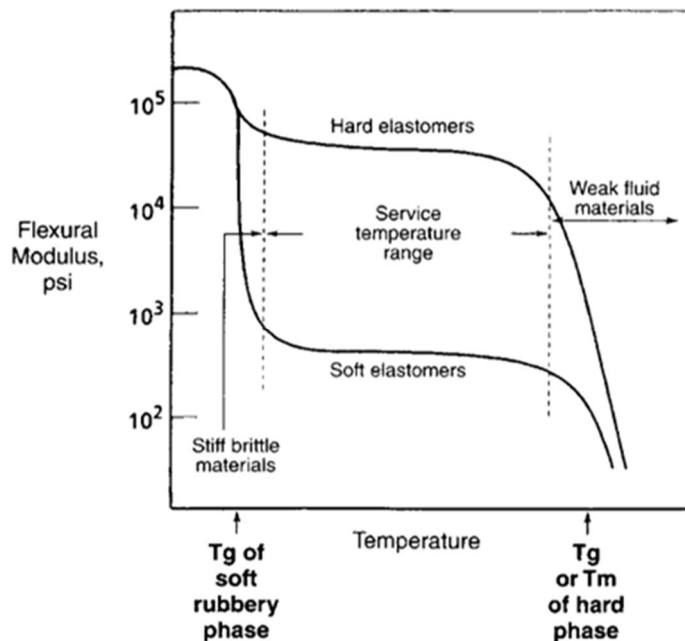


Figure 2.2. Flexural modulus as a function of temperature for thermoplastic elastomers [1].

It can be said as a generalization that the two-phase system gives TPEs their unique properties. In order for the phases to function right their solubility has to be at a right level. They cannot be so soluble that they blend forming one homogenous phase. Nor can they be so incompatible that they do not wet. Most TPEs are more soluble than is

necessary and some mixing occurs. Some factors contributing to phase separation are highly different structures between two phases, high molecular weight or long polymer chains, and low processing temperatures. [1]

2.2 Types Used for Foaming

Thermoplastic elastomers can be divided into groups according to their structure or base materials. Names of the groups differ depending on the source but groups stay essentially the same. In this thesis naming and grouping is done according to standard ISO 18064, in which nomenclature and abbreviated terms of TPEs are defined [4]. Most TPEs have been successfully used in foaming, and in this thesis we only discuss the ones that have been found foamable with present techniques. Some comparison between properties of TPE groups can be found in Appendix 1.

2.2.1 Styrenic Thermoplastic Elastomers TPS

Styrenic thermoplastic elastomers (TPS) are type A-B-A block copolymers where two hard segment (A) are connected to each other by a soft segment (B). In styrenic block copolymers the hard segment is polystyrene and the soft is an elastomeric material which differs according to the material in question. The most commonly used TPSs are

- styrene-butadiene-styrene (SBS) with polybutadiene as an elastomer
- styrene-isoprene-styrene (SIS) with polyisoprene as an elastomer and
- styrene-ethylene-butylene-styrene (SEBS) with ethylene-butylene as an elastomer.

Also other TPSs are used commercially, but they are used far less. Of the three mentioned, SBS and SIS have similar properties and SEBS differs because it is hydrogenated and has a saturated elastomer structure. The structure of a SBS was shown in Figure 2.1. [1, 2]

SBS and SIS both have double bonds in their original monomer unit which give them lowered resistance to chemicals, such as oils and solvents, oxidation and high temperatures. These properties can be enhanced to a certain point by additives. Though they do have good wear resistance and electrical properties and also come in wide hardness range, it is highly unlikely that they could be considered for this application. SEBS however has a saturated structure which means that it has been hydrogenated and has no double bonds. This makes the material more stable and additives can be used to give it wider range of properties. That being so SEBS, like other TPSs is typically used blended with other polymers or at least filled with additives. In her thesis work Miettinen studied a SEBS material and found it had good enough properties to be considered as a material for gaskets. [1-3, 5]

2.2.2 Thermoplastic Rubber Vulcanizates TPV

Thermoplastic rubber vulcanizates, also vulcanisates, (TPV) are polymer blends consisting of thermoplastic and highly vulcanized rubber. In an ideal case the elastomer phase is dispersed as finely divided, ca. 1 μm in diameter particles and the amount of thermoplastic is relatively small. When the material is then heated, thermoplastic melts and allows rubber particles to move easily in the melt. TPVs are prepared by a process called dynamic vulcanization where rubber is vulcanized during mixing process of the polymer blend. The degree of crosslinking is usually close to 100 %, which is essential since the complete vulcanization of rubber phase gives TPVs their almost rubberlike properties. [1, 6]

The most common TPV is a blend of ethylene-propylene-diene monomer (EPDM) and polypropylene (PP). A large variety of rubbers and semi-crystalline thermoplastics can be used in TPVs but only a small portion of those pairs are useful in practical purposes. A suitable pair has to have surface energies that match and the thermoplastic has to be at least 15 % crystalline. Some other thermoplastics used are polyethylene terephthalate (PET) and polyethylene (PE), and rubbers respectively nitrile rubber (NBR) and isobutylene-isoprene (IIR). [1, 6]

Properties of TPVs are as good as or even better than TPEs based on block copolymers. In comparison TPVs demonstrate better mechanical properties, fatigue resistance and melt stability. They also show less swelling in oils, improved utility in high temperatures, and more reliable processing characteristics in processing. It has been found that these improved properties are the result of rubber particles forming a network during cooling of the material. [1]

2.2.3 Olefinic Thermoplastic Elastomers TPO

Olefinic thermoplastic elastomers (TPO) are blends of polyolefins, usually PP, and a non-vulcanized rubber, usually ethylene-propylene copolymer (EP) or EPDM. There are two opinions on how to classify TPOs. Some consider TPOs to be divided into non-vulcanized and vulcanized materials. Thus TPOs would include TPVs based on polyolefins. The predominant opinion, also defined in ISO 18064, is that TPOs can be only lightly or not at all cross-linked [4]. In this thesis TPOs are covered according to the latter. [1, 6, 7]

Structure of TPOs is quite similar to TPVs. The biggest difference is that in TPOs the rubber phase is not vulcanized thus enabling deformation and rupture during processing. In addition, rubber can form a continuous phase or the structure can be co-continuous. Co-continuous phase is illustrated in Figure 2.3. [1, 6]

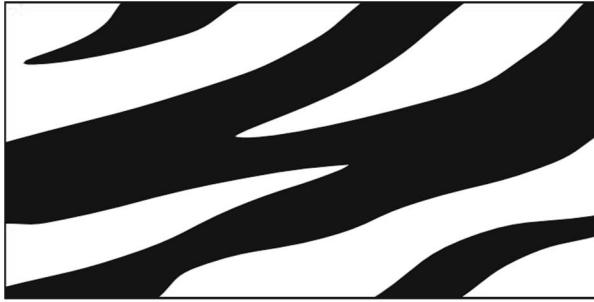


Figure 2.3. Illustration of a co-continuous phase.

Like with all materials properties of TPOs vary greatly depending on base materials and structure. Because of their non-vulcanized structure TPOs have very good processing characteristics and a smooth surface. The added rubber phase gives material impact strength and crack resistance in low service temperatures, which make it a good material for car bumpers and air bag covers. They resist ozone, light and weather relatively well but their oil resistance is only fair, which is why for this application they were not considered further. [1, 6, 8]

2.2.4 Urethane Thermoplastic Elastomers TPU

Urethane thermoplastic elastomers (TPU) are block copolymers consisting of rigid and flexible segments. The soft segments can be either polyesters or polyethers, which have high molecular weight. If a segment with low molecular weight is added instead, the material becomes rigid. The soft and hard segments in TPUs have different polarities, causing separating during cooling, thus forming clearly different phases. [2, 9]

TPUs are strong and tough materials and have a good ozone and oxygen resistance. Some of their properties are characteristic only to other of the possible soft segments. Polyester based TPUs have a good oil and hydrocarbon resistance, while the polyether based TPUs are more suitable for wet conditions. TPUs are also quite expensive and their hardness range is from medium to hard, which reduces possible applications. Their use is quite diverse from car body components and hydraulic hoses and seals, to fabric coatings and shoe soles. [2, 10]

2.2.5 Copolyester Thermoplastic Elastomers TPC

Copolyester thermoplastic elastomers (TPC) are multi-block copolymers. Structurally they are copolyether esters with alternating and random-length sequences, which are either long-chain or short-chain oxyalkylene glycols, connected by ester linkages. The soft segments are usually short chain ester units and the hard segments are long ether or ester units. As their structure, also their properties mostly resemble TPUs.[1, 2]

TPCs are tough materials with good impact resistance. They have good resistance to ozone, oxygen and oil. Like TPUs they have a limited hardness range and high cost. The ratio of soft and hard segments can be controlled thus the properties can be modified

e.g. from soft to hard materials. In her work Miettinen stated that polyether ester elastomers have very good oil resistance but their hardness is too great for gaskets. [1, 5]

2.2.6 Thermoplastic Elastomers from Recycled Materials

Use of recycled materials has some of the same motivation as foaming. The idea is to reduce material costs and lighten the environmental burden of the industry. In foaming environmental aspect is achieved with reduced need of raw materials and transportation. With plastics the cost aspect does not fully apply as long as raw materials, such as oil, are easy to get and the prices stay low.

Like other thermoplastics TPEs can be produced from recycled materials, but in addition to recycled plastic, waste rubber is used. The elastomeric phase can consist of recycled material only or it can be used in addition to virgin elastomer. Waste rubber can be used simply ground meaning that it still has its vulcanized structure or it can be devulcanized. In devulcanizing crosslinks are severed but at the same time damage is caused to polymer chains, thus affecting mechanical properties. When melting and remoulding thermoplastic materials, a portion of the mechanical properties is always lost and also discoloration and cross-linking are possible. This is why polymeric materials cannot be recycled indefinitely without severely compromising properties and recycled materials are seldom used alone. [1]

Often when mixing thermoplastics and waste rubber the achieved materials are more like impact-resistant thermoplastics, but also true TPEs have been achieved [11]. Recycled rubber can also be mixed with TPEs resulting in materials varying from impact-resistant thermoplastics to TPEs. Rubber can be used ground as more like filler, or it can be used to replace some of the virgin rubber. Adding ground waste tire has been found to enhance certain properties such as compression set and tear strength in SEBS, and usually up to 50 % of the virgin elastomer can be replaced with recycled material. [1] Blending recycled plastic with recycled rubber is quite rare, since it puts together the decreased properties of both materials. However, TPE material can be achieved from 100 % recycled material, but the properties differ from materials produced from virgin base materials. [12]

3 THEORY OF FOAMING

Foaming means creating gas filled cells inside a material. Plastic foams can also be called cellular or expanded plastics. There are several different ways of foaming and they can be divided into physical, chemical, mechanical, and syntactic foaming. In physical foaming gas or low-boiling liquid is mixed into the material. Foaming is based on a change in physical state of the gas or liquid. In chemical foaming chemicals are added to the material. In right conditions chemicals react forming gas which nucleates into bubbles. In mechanical foaming the gas is whipped to the material as such, like in making whipped cream. It is a method rarely used and will not be covered in this thesis. Syntactic foaming means introducing gas-filled spheres into the material. Expandable microspheres are tiny plastic balls filled with gas. In right conditions during processing the gas expands forming a thin-walled cell. Because of the amorphous structure in all polymers, in time the gas will diffuse to the surface of the material and air will replace the evaporated gas in the cells as the system tries to reach equilibrium with atmosphere. This happens to all foams regardless of the foaming method. Foaming in general is used to reduce the product density thus cutting material cost and weight, but it also enhances thermal insulation and improves dimensional stability. [9, 13]

3.1 Structure of Foams

As said before, structure of foams consist of at least two phases, solid plastic matrix and gaseous cells. There can be more than one solid state, meaning that fillers and fibres can be used as well as TPEs. It is critical that gas cells remain certain size, which ever size, or sizes are preferred and spread uniformly throughout the material. In reality no foam consists only of one size cells and the important thing is to keep the size distribution narrow.

Cellular materials can be categorized into closed and open cell foams. With closed cells, cells can be close to each other but there is always a plastic phase between them. The material stays air-tight. In open cell structure, cells are connected to each other and the plastic between them has ruptured allowing air to flow through the material. Normally foams contain both open and closed cells and the important factor is their ratio. [14]

In chemical and physical foaming foam formation involves nucleation of gas cells in the polymer melt, growing of the cells and cell stabilization by increasing viscosity of the matrix. In the first stage of foam formation small spherical gas cells nucleate in the material. In the second stage cells start to grow as more gas flows into them from a gas saturated matrix or smaller cells. As cells grow their walls keep approaching each other,

creating a close packed structure but still remaining spherical. In the third stage, when the cells keep growing their walls touch and they start to lose their spherical form, gaining a more polyhedral form. In the fourth, and last, stage, if cells still keep growing walls between them rupture forming an open celled structure. Cell growth can be stopped at any stage by cooling the material, which is one way how different structures can be achieved. The stages of foam formation are illustrated in Figure 3.1. [14, 15]

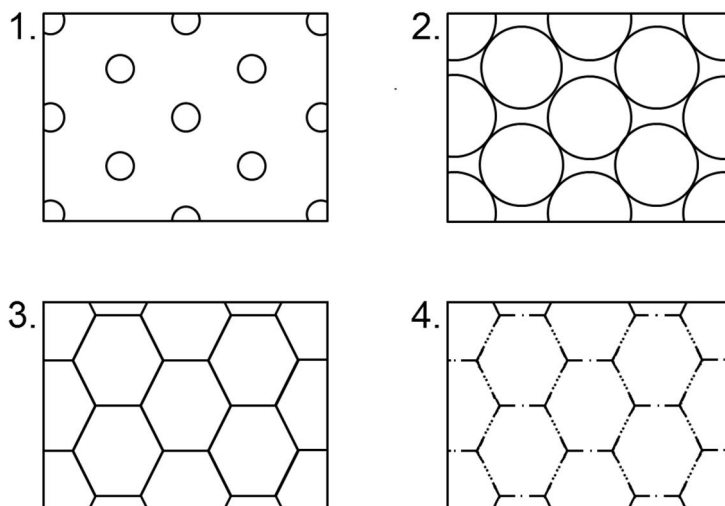


Figure 3.1. Stages of foam formation: 1. Cell nucleation. 2. Cell growth, spherical cells. 3. Change into a polyhedral structure. 4. Change into an open-cell structure.

Foams can be categorized by the size or quantity of cells, and foam properties depend a lot on both of them. By density, usually kg/m^3 , cellular materials are divided into low and high density foams. In reality this division is too rough, and a more precise way is to divide foams into five classes, which are

- very light ($3 - 50 \text{ kg/m}^3$)
- light ($50 - 200 \text{ kg/m}^3$)
- medium ($200 - 500 \text{ kg/m}^3$)
- heavy ($500 - 700 \text{ kg/m}^3$)
- super heavy ($>700 \text{ kg/m}^3$).

In low density foams a great drop in density and weight has been achieved. The quantity or size of the cells has to be great to produce low density foams. High density means that most of the weight has remained after foaming. [16]

Mechanical strength properties are mostly proportional to foam density. High density foams are usually used in load-bearing applications while low density foams are used in e.g. insulation. When comparing foamed and solid materials, a more descriptive property is relative density, which is the ratio of foamed and solid material. [15, 16]

For a long time it was thought that the minimum cell diameter was several dozen micrometres, but when the resolution of microscopes improved much smaller cells were found. The minimum diameter of these cells was less than a micrometre. Nowadays it is possible to control cell formation enough to create only these small cells, called micro-

cells. The method of producing them is called microfoaming, respectively. Cell sizes considered as microcells differ depending on the source, but most have the maximum of 70 or 100 μm . Microfoaming is widely used and will be further discussed in Chapter 4.4. Cellular structures that have a cell size smaller than microcells, preferably under $1\mu\text{m}$, are called nanofoams. The research on nanofoams is still in its beginning and is done only on laboratory scale. Various methods have been used, often using gas as blowing agent (BA) and controlling cell growth with the molecular structure of the material, or gas solubility and viscoelasticity differences between different phases in the material. Cell sizes of 0.5 nm at smallest have been achieved, but as nanofoaming is still in laboratory state and it not be further discussed in this thesis. [16, 17]

3.2 Effect of Foaming on Properties

Properties of plastic foams are dictated by properties of the material but also by properties of its cells, more clearly cell structure. Different materials with different apparent and cell densities cannot be directly compared, but generalizations can be made. As the focus of the thesis is on mechanical properties, no other properties such as thermal or sound insulation will be discussed.

Foaming often deteriorate tensile properties of the material. This is due to the decreased density of the material. Wong et al. studied the effects of processing parameters on foam structure and mechanical properties during TPO microfoaming. They found that decreased relative density causes decreased tensile strength but increased elongation. For tensile modulus the effect was not as straight forward, but as density dropped tensile modulus first started decreasing until it again increased after reaching 0.9 relative density. [18]

When foaming flexible materials, TPEs included, it has been found that increased cell size lowers hardness. Nema et al. found that when chemically foaming, hardness of TPU decreased from 85 to 55 ShA with density reduction of 34 %. A similar drop for gaskets would be desired. [9]

Surface defects almost always occur during foaming. They are normally caused by premature cell formation, and can be affected by adjusting processing parameters. Tiger stripes are most common defects found on thermoplastics. They are not only a problem with foaming but also with solids, PP/rubber/talc blends as an example.[19] They are stripes of different grades of gloss or shine, appearing perpendicular to the flow direction. Guo et al. found that when chemically foaming TPOs, instead of tiger stripes silver streaks were found. In addition to adjusting processing parameters, it was found that using branched PP instead of linear produced parts with less defects.[20]

4 FOAMING METHODS

Foaming is mostly done by chemical, physical or syntactic foaming. Chemical and physical methods are both based on blowing agents (BA), which are mediums for liberating gas into the system. These methods create cells that have walls of the matrix polymer. Syntactic foaming is based on separate gas filled spheres, usually polymer of glass, which are mixed into the material. Some polymer spheres can expand as thermal conditions become suitable during processing, creating spheres with very thin walls. These are called expandable microspheres and they are the only way of syntactic foaming discussed in the thesis. [16]

4.1 Physical Foaming

Physical blowing agents (PBA, also physical foaming agents PFA), form gas by undergoing a change in physical state. They are usually inert gases, which are dissolved in the polymer in molten state, or liquids that have a low boiling point. In addition solid PBAs are used, but only for thermosets and rubbers. It is crucial for successful foaming that the PBA completely dissolves in the molten polymer. Dissolution depends on solubility of the blowing agent, saturation pressure, degree of mixing and residence time. [7, 21]

4.1.1 Gas as a Physical Blowing Agent

Using gas as a PBA in foaming is based on diffusion. The material is first saturated with gas under high pressure, and when pressure is reduced gas diffuses out of the matrix material and foaming occurs. Gases used this way include nitrogen (N_2), carbon dioxide (CO_2), butane, hydrogen, helium and many others, but mainly N_2 and CO_2 are used. [16]

Carbon dioxide is the most used BA, when considering its use in all its states. It is cheap, safe to use, abundant and environmentally safe, even though it is a greenhouse gas. It also has high solubility to polymer melts, which enables high saturation in low pressures, but slows down the rate of pressure drop. This causes cells to expand for too long and cell size is harder to keep small. The problem emerges mostly in foaming of large size products. Also contributing to the wide use are the critical temperature and pressure, which are needed to achieve a supercritical fluid used in making low density or microcellular foams. For CO_2 these values are 31 °C and 7.38 MPa as for N_2 they are -146.9 °C and 3.4 MPa, respectively [14]. A more detailed comparison between the two PBAs can be found in Appendix 2. [13]

Nitrogen has some of the same advantages as CO₂. It is safe to use, cheap and abundant, not to mention environmentally safe, as it is merely borrowed from the atmosphere. In addition it has some advantages when compared to carbon dioxide. If foams with same weight percentage of PBA are studied, it is found that with N₂ a higher cell density and expansion ratio has been achieved. N₂ foamed products also shrink less, since it is the main component in atmosphere and the diffusion in and out of the material is almost equal. The downside is that N₂ has low solubility in polymer melts, and because of this its use is mainly limited to microfoaming. [8]

4.1.2 Liquids and Solids as Physical Blowing Agents

Low-boiling liquids liberate gas into the system when temperature is increased or pressure reduced, or both. The temperature can be applied outside the system or from exothermic reactions, such as polymerization, inside the system. Many liquids are used, hydrocarbons, alcohols, ethers and ketones among others. [14]

One of the most used liquid group is halogenated hydrocarbons, and among them most importantly **chlorofluorocarbons** (CFC), also Freons. They were widely used for production of polyurethane, PE and PS foams. Their advantages were incombustibility, low toxicity, low diffusion coefficients in polymer melts, and low coefficient of thermal conductivity which allowed the foaming to be controlled precisely. However CFCs were discovered to react with ozone in the stratosphere, which causes ozone depletion and enables harmful ultraviolet radiation to get through. CFCs also contribute to the greenhouse effect. This is why there have been legislative measures taken to reduce and finally stop the use of CFCs. In Montreal Protocol it was stated that the use of CFC should be slowly run down, and fully stopped by 1996, and in the case of a less harmful hydrochlorofluorocarbon (HCFC), by 2030. This has given the industry a jolt to continue developing more environmentally safe PBAs. [16, 22]

The most eligible substitute for CFC is **aliphatic hydrocarbons**, including various pentanes. They have low cost, are environmentally friendlier and are compatible with most polymers. They do not offer as good foamability as CFCs, but mostly reach the same levels as HCFCs. Hydrocarbons also have their own disadvantages. Firstly, they do have their own impact on the environment. They are under emission control, which means that their use is limited, especially in heavily populated areas. Secondly, hydrocarbons are highly flammable and explosive, which means that in order to use them, investment to machinery and work conditions have to be made. The extent of changes depends on the local regulations, but at least improved ventilation and alarm systems should be installed. [14]

Water has not been used long as a PBA, but it is under a lot of research and has been found viable in TPE industry, especially when foaming TPVs. The biggest advantages of water are its low price, abundance, and environmental impact. However it has certain special characteristics among PBAs. Water has low volatility and solubility when compared to other PBAs, but it also enables the use of lower pressures during

foaming, can be used as a non-pressurized liquid and permits good metering accuracy. [14, 23]

Solids are not exactly PBAs but more like PBA-sorbents. The solid is first saturated with gas or low-boiling liquid under pressure and during foaming nucleation is initiated with increasing temperature. Gases used this way include methylene chloride, chloramine and acetone, whereas most liquids mentioned before can be used. The solid material can be carbon, clay or silica gel, among others. Solids are only used for thermosets and rubbers, and for rubber production they have an advantage compared to others. Using ultra-microporous carbon saturated with CO₂ ensures foaming under vulcanizing conditions. On a downside, only high density foams with heterogeneous cell structures can be achieved by the method. [16]

4.1.3 Nucleating Agents

Nucleating agents are used with PBAs to enhance homogeneous cell nucleation. This means narrow cell size distribution and a constant cell density. Nucleating agents can be gases that produce supersaturated solution before the use of a PBA, fine powders that act as solid surfaces for cell nucleation or chemical blowing agents (CBA, discussed in the next chapter). In case of powders the nucleating agent remains thermally stable during the foaming process, whereas CBAs undergo a chemical reaction. Usually the CBAs used this way are based on endothermic reaction, such as blends of citric acid and sodium bicarbonate. The gases are mostly the same as the ones used as PBAs, and include CO₂, N₂ and air. The powders can be talc, silicon dioxide or calcium stearate, among others. [14, 16]

With TPE foaming the nucleating agents are usually powders, especially talc has been used. In 2010 research of Kim et al. it was noticed that when using low PBA concentrations the adding of talc content increased cell density, but with high PBA concentrations the talc content did not have the same effect. [8]

4.2 Chemical Foaming

Chemical blowing agents (CBA, also chemical foaming agent CFA) are chemicals that react in high temperatures releasing gases which trigger the foaming process. CBAs are most often compounds containing more than one element. These elements are accelerators, which control the reaction rate, and cell regulators, which control the cell structure. The reaction can be reversible or irreversible decomposition, or a reaction between two elements. In order to be used, CBAs have to be stable enough not to react under normal processing conditions, only at the highest temperatures of the process. CBAs are typically more expensive than PBAs, which is why they are rarely used to produce low density foams. Though the chemical itself is expensive, CBAs do not often require investments on processing machinery like with PBAs, and can be processed with almost all existing polymer processing techniques. They are most often powders that do not need special storage or handling equipment, and can be just added in a hopper or they can be

readily mixed to the material as masterbatches. It is also common to use more than one CBA at the same time to achieve a required structure, for example a mixture of endothermic and exothermic agents. [13, 14, 16]

4.2.1 Endo- and Exothermic CBAs

CBAs can be divided into two groups according to their reaction heat. Endothermic CBAs absorb heat while decomposing, while exothermic CBAs release heat. This affects the melt temperature only slightly, but the reaction greatly. A comparison between the two CBA groups is shown in Table 4.1.

Table 4.1 Comparison between endo- and exothermic CBAs [13].

Properties	Exothermic	Exothermic plus Endothermic	Endothermic
Density reduction	Excellent	Very good	Good
Cell structure	Coarse	Medium	Fine
Colour	Yellow	Pale yellow	White
Discolouration	Yes	Small amount	None
Odour	Pungent (NH ₃)	Fair	Little
Gas	N ₂ (plus others)	Mainly N ₂ /CO ₂	CO ₂
Environmental impact	Low	Low	Little or none

The reaction of **exothermic** CBAs is difficult to control, and once it starts it is difficult to stop before all the agent has reacted. This is why they usually generate more gas and therefore create higher pressures, which make them ideal for foaming processes that need the pressure but the cell structures are usually heterogeneous. Azodicarbonamide (ADC) is the most used CBA in the world. It is exothermic and used on its own and in blends. During decomposition it releases mostly N₂, but also CO₂, carbon monoxide and ammonia. ADC is a yellowish powder and produces white or off-white residue during decomposition as well as solid products, including biurea and cyamelide, which can cause plate out. [13, 14]

Endothermic CBAs produce foams with smaller cell sizes, better mechanical properties and more controlled processing. They also show less discoloration and are considered safer. On a downside they do need more energy for processing, thus requiring longer cycle times. Of endothermic CBAs, sodium bicarbonate is most widely used. It is inorganic, opposed to organic, which most CBAs are. During decomposition it yields CO₂ and water, and therefore cannot be used with polymers that degrade in the presence of water. [21]

4.2.2 Choosing a CBA

When choosing a right CBA for the material and processing technique a few factors have to be taken into account. Firstly, processing temperature has to be compatible with reaction temperature of the CBA. The reaction has to take place when polymer reaches the right viscosity. Activators, which lower the reaction temperature, can be added to

widen temperature range. Secondly, the amount of gas liberated during reaction has to match the desired foam density and gas itself has to be compatible with the material in question. As mentioned before in the PBA chapter, different gases are more compatible with different materials and produce different cell structures. This rule applies with CBAs as well as PBAs. Like ADC, some CBAs yield by-products that can cause degradation in unsuitable polymers. The by-product is usually water, but can also be ammonia, or alkaline or acidic gas. Thirdly, reaction rate has to match the process and influence of the reaction heat, endothermic or exothermic, on the process should be taken into account. A comparison between various CBAs can be found in Appendix 2. [14]

4.3 Expandable Microspheres

Expandable, also expanding, microspheres are small polymer spheres with hydrocarbon inside. When heated, polymer softens and pressure of the gas increases. If external pressure is high spheres remain small or only expand slightly. When external pressure drops, as when material is injected to a mould, spheres expand to a volume of 40-70 times their unexpanded volume. Figure 4.1 illustrates the change in microspheres upon expanding. [24]

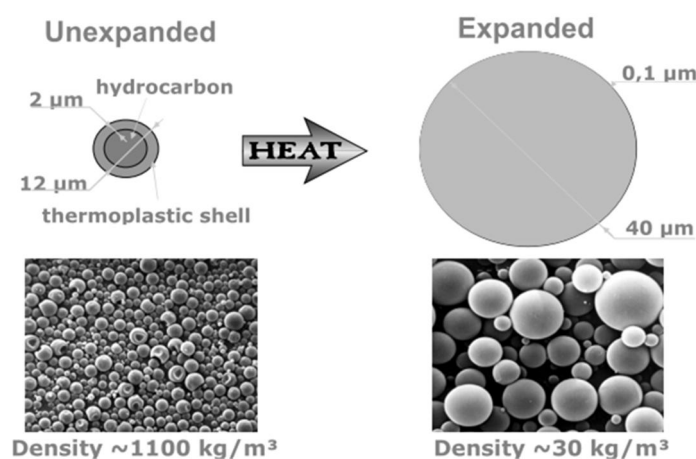


Figure 4.1. Illustration of expandable microspheres unexpanded and expanded [24].

Expancel® is the trade name of expandable microspheres from AkzoNobel. They can also be found with other trade names, e.g. Advancell® from Sekisui, but Expancel is the microsphere supplier selected for the thesis. The technique for producing the spheres was originally developed by Dow Chemical Company.

4.3.1 Materials and Properties

In order to keep gas inside the spheres shell material has to have good barrier properties. Expandable microsphere shells are made of copolymers with varying properties to be used in different conditions. Also the hydrocarbon varies between different grades. This way the most suitable microsphere grade can be chosen to a diverse group of applica-

tions. If a polymer with low processing temperature is used as a matrix, a hydrocarbon with high saturation pressure and a shell polymer with low T_g are used in microspheres. If the matrix has a high processing temperature, hydrocarbons with long carbon chains and polymers with high T_g 's are used, respectively. According to Whinnery, [25] Expanding microspheres they studied were made from polyacrylonitrile (PAN) and polymethacrylonitrile (PMAN) and the gas inside was iso-pentene. [24, 25]

Expandable microspheres are produced by a method called suspension polymerization. Monomers, from which the copolymer shell consists, and the desired hydrocarbon are mixed and then dispersed in water. The dispersion is then heated with an oil soluble activator to start polymerization, during which the monomers bond creating polymer spheres simultaneously encapsulating the hydrocarbon inside. During polymerization the dispersion is stirred or shaken. Average size of cells can be controlled by changing the recipe and mixing speed of the dispersion. After manufacture spheres are screened and divided into different size groups. This way it is possible to control cell size in the final product even better. [24-26]

A greater variety of polymers can be foamed with expandable microspheres than with other foaming methods. This is because the gas is encapsulated inside the sphere material, which means that the matrix itself does not need to be capable of sustaining wall structures. What is required from the polymer is that it can be melt processed and that its processing temperature is low enough to allow the use of microspheres. If temperature is too high, microspheres break down and collapse. The highest processing temperature for the high temperature grade spheres is 260 °C, but most of the spheres should be used in temperature of 200 °C or less. The lowest possible temperature is 100 °C for the low temperature grades. Plastics with low shear viscosity are easier to foam but no limiting value has been given. Some of the thermoplastics that can be used include PE, PP, polystyrene (PS), ethylene vinyl acetate (EVA), and polyvinyl chloride (PVC). The possible TPEs have all been introduced earlier in this thesis and are TPS, TPU, TPO and TPV. TPEs are a little more unpredictable to foam because of their complex structures and higher viscosities. It is more difficult to predict changes in foam structure when changing processing parameters and more optimizing is needed. All foamable materials can also contain glass or wood fibres, nano particles, or calcium carbonate (CaCO_3). [24, 27]

In addition to decreased weight and density, expandable microspheres offer improved thermal and sound insulation, shock and vibration absorption, and anti-slip. They also improve surface aesthetics and improve dimensional stability. Mechanical properties, like tear strength and elongation, are reduced like with all foaming methods, though the relative values, which take the density drop into account, mostly stay the same. In Expancel trials it was found that TPU lost 15 – 30 % of its tensile strength when the density decreased by 40 – 50 %. For SEBS the drop in tensile strength was 80 %, respectively. [24]

With injection moulding expandable microspheres are typically used for thick and simple parts, and their most important foam applications are shoe soles and synthetic

wine stoppers. Extrusion is used to manufacturing cables, hoses and profiles for automotive and construction industries, allowing a more complex profile than injection moulding. With polymers expandable microspheres are usually used for foaming, but can also be used as light weight fillers. The spheres were first developed for paper industry, where they are still mainly used as fillers to increase bulk, which means higher stiffness with low weight. [24, 25]

4.3.2 Processing Methods with Expandable Microspheres

Manufacturing foamed products with expandable microspheres is possible with most plastic production methods. They can be incorporated into extrusion, injection moulding, film blowing, thermoforming, rotational moulding and calendering. Microspheres are often used with CBAs to form foam with optimal expansion and even cell structure. [27]

During **injection moulding** microspheres do not expand before being injected to a mould. Pressure inside the cylinder is too great and is relieved only after the nozzle. Expandable microspheres do not require much from the injection moulding machine itself. A nozzle with needle valve, a shut-off nozzle, is preferred but it is not imperative. Its purpose is to prevent leakage and pressure drop inside the cylinder and thus enhance the reproducibility. If the maximum temperature of microspheres is reached during processing, it should only be for a short time right before injection. Cycle time is preferred short and cooling time can be reduced in comparison to solid parts. If cooling time is long, screw should not be filled up until just before the next injection. Also injection speed needs to be high enough to ensure fast filling of the mould but low enough not to cause too much friction heat. [24, 28]

Though requirements for the machine are minor, more is demanded from the part. The part geometry should not be too complex and thin walls should be avoided. A wall thickness less than 3 mm does not allow enough space for sufficient expansion. If a part has varying wall thickness with thin wall sections, sections foam differently causing density variation throughout the product, which leads to different properties within the part. There can also be problems when manufacturing big parts, when cooling in the middle might take so long that the spheres start to collapse. The maximum thickness varies depending on the material and processing temperature. [24, 28]

In **extrusion** microspheres expand after they have been extruded through a die. More is demanded from an extruder than an injection moulding machine. Firstly, the L/D ratio should be 32 or less. Pressure within the cylinder prevents spheres from expanding prematurely and thus vacuum or venting zones are not recommended and must be plugged if a machine has them. An open vent allows pressure to escape and spheres to expand, making the end product poor quality. [24, 29]

As with injection moulding, during extrusion the time spheres are subjected to high temperatures should be kept as short as possible. If residence time is too long, shells will start to deteriorate and the gas escapes. Also likewise temperature should be lower at the hopper and highest right before the die. More importantly die temperature should

be optimized as it has a greater effect on foam formation than barrel temperature. Haul off speed needs to be adjusted to keep the dimension of the profile constant. It is important to notice that melt strength of the foamed material is not as great as with solid, so speed should not be increased sharply. Cooling can be enhanced as it ceases cell growth and therefore quick cooling gives the profile a smoother surface. If even smoother surface is needed, a solid surface layer should be co-extruded. [24, 29]

4.4 Microfoaming

Foams which have an average cell size of 100 μm or less are considered microfoams. The original reason for developing methods to generate microcells was to create cells with diameter smaller than the critical-flaw size. Smaller cells would not, in theory, cause much deterioration in mechanical properties. And indeed this was achieved. While mechanical properties of microfoamed materials are often lower than of solids the relative properties, which take the density reduction into account, usually rise. Light to heavy foams can be achieved by microfoaming, and it has been noted that with microcells cell size is almost independent on foam density. Even with low density foams cell size remains quite small. Microfoams are usually spherical and closed cell foams, but there has been interest in creating open celled structures as well. [14, 16]

Microscale cell structures can be achieved with most foaming methods. Chemical and physical foaming agents can both be used in injection moulding and extrusion. Also expandable microspheres can be expanded to a size that is still considered microcell. The first method developed for microfoaming was the solid-state batch process. Even though it was the first one developed and fairly slow, it is still used actively in laboratory conditions. More advanced way of physical foaming was originally invented in MIT and commercialized by Trexel. It is called the MuCell® process and it is covered in Chapter 4.4.2. Other methods include Optifoam™, Ergocell® and ProFoam®, which were covered in the thesis of Ahola. [16, 30]

4.4.1 Solid-State Batch Process

With solid-state batch process it is possible to form a part with solid skin and evenly distributed cell structure. There are two different ways for solid-state foaming. The first one is called temperature soak process, and it consists of two stages. First the material is placed in a vessel with high pressure and a non-reacting gas, usually CO_2 . Temperature is kept moderate, mostly room temperature. In time gas diffuses into the material and spreads uniformly. When the part is taken out and brought into atmospheric pressure it is thermodynamically unstable. The part is then put to a heated bath with temperature control and heated to a certain temperature above its T_g . The dissolved gas allows cells to nucleate and grow in the solid state, which is why materials formed this way are called solid-state foams. The other way of solid-state foaming is the pressure quench method, where cell nucleation is achieved by a sudden pressure drop. In this method

gas-saturated part is already in high pressure and a temperature above T_g . Pressure is then released which evokes cell nucleation and growth. [13, 14]

4.4.2 MuCell®-Method

The MuCell®-method allows microfoaming during extrusion, injection moulding, and blow moulding. The parts have a solid skin and an even cellular structure. The method is based on controlled use of gas as supercritical fluid (SCF). Supercritical fluid is achieved by applying a high pressure to a gas in elevated temperature. Both pressure and temperature have to be above the critical values specific for each gas. A table with critical values for CO₂, N₂ and O₂ can be found in Appendix 2. In supercritical form gas has elements in gas and liquid state at the same time. These fluids have a low compressibility of liquids, and high diffusion rate of gas. The only gases used with MuCell are CO₂ and N₂, and of these N₂ is used more often, since wall thicknesses are kept small and the amount of PBA in the solution are low. These enable the use of more aggressive but poorly soluble N₂. [21, 31, 32]

MuCell enables foaming for parts with wall thickness of 0.5 mm or more. The method is mostly used for thin walled parts and 3 mm has been considered the maximum wall thickness. Also thicker parts can be foamed with MuCell, but cell sizes cannot be controlled the same way and cells grow larger. Physical foaming typically enables the use of more difficult part geometries. The use of a PBA reduces shear viscosity of a melt, and it is possible to fill moulds that were not possible before or with fewer gates. If a high viscosity reduction is wanted, CO₂ should be used as PBA, since up to four times as much of CO₂ compared to N₂ can be dissolved to the polymer melt. With the MuCell method also sink marks can be avoided, since internal pressure acts as hold pressure. As foaming reduces density, it can be presumed that fire resistance drops accordingly. However, when foaming parts with wall thickness of 2 mm or more using MuCell, usually V-0, V-1 and V-2 ratings of the materials are kept even after foaming. Materials with 5V -rating always experience a drop in rating. [21, 32]

As mentioned before a separate unit is needed for this method. The unit consists of a SCF delivery system, a special screw and a shut-off nozzle. The SCF delivery system consists of plasticizing cylinder with gas injectors and a gas unit for the SCF. The special screw needs to have a plasticizing section and a subsequent mixing section. Also an accumulator for fast injections may be needed for some part geometries. [21, 31]

In MuCell injection moulding process the thermoplastic must first be homogeneously melted in the plasticizing section. The SCF is then precisely injected to the barrel and into the melt. In the mixing section of the screw SCF disperses and dissolves evenly and a homogenous solution is achieved. During injection pressure drops enabling nucleation of cells, which then start to expand by diffusion of gas into the cells. Cell size grows until the viscosity of the material becomes too great during cooling. [21]

5 RHEOLOGY OF FOAMING

The term rheology rarely comes to mind at first when talking of foamability of polymers. This is a contradiction, since rheological properties greatly affect the processing and foam formation. In order to understand foaming and to perfect the processes a certain understanding of the materials rheology needs to be achieved.

The discussion of rheology in foaming can be roughly divided into two interconnected fields: the effect of BAs on the viscosity and the effect of rheological properties on cell nucleation and growth. The addition of BAs changes the needed processing parameters but also has an influence during the cell formation, when rheological properties play a significant role. Both of these perspectives are important in understanding the foaming process and are therefore discussed in more detail. It should be noted that the effects discussed here do not apply to syntactic foaming.

Foaming thermoplastics and TPEs differ greatly in this field. The basic principles, of course, stay the same but the two-phase structure of a TPE makes the phenomena more complex and therefore harder to understand. There are also some difficulties in measuring viscosities of polymer/BA solutions, since the pressure has to be high enough for the gas to stay diffused.

5.1 Brief Introduction to Rheology

In order to discuss rheology of foaming, certain fundamentals of rheology have to be understood. In this chapter the rheological phenomena are gone through in their simplest forms. A lot of different models have been introduced to explain rheological phenomena, ranging from overly simplified to very complex, but in this work only the basic principles are covered. There are also various ways to calculate values for rheological properties from the models, and the ones used in the experimental part will be introduced in Chapter 8.

Polymers are viscoelastic materials, meaning that they exhibit both elastic and viscous behaviour. Elastic deformation is time-independent and reversible. When stress is applied to an elastic material the corresponding deformation occurs instantly, and when the stress is then removed the material returns to its former state. Viscous deformation is time-dependent and irreversible. When applying stress, a viscous material deforms in process of time until the stress is removed, and the deformation is permanent. Viscoelasticity means that some of the deformation is elastic and some of it is viscous. When applying stress to the material, some deformation occurs instantly and in time more deformation will take place. When stress is removed, the same amount of deformation as

occurred instantly will be reversed. The rest of the deformation is permanent. The different deformations are illustrated in simplified form in Figure 5.1. [33]

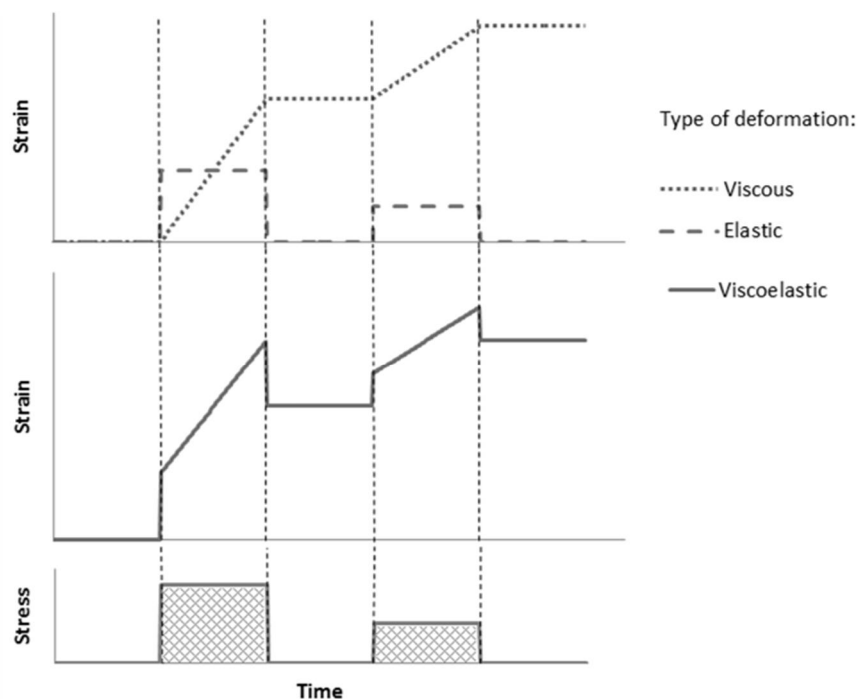


Figure 5.1. A simplified illustration of three types of deformation: Viscous, elastic and viscoelastic.

The viscoelastic behaviour of the figure does not fully correspond to the reality, but is a representation of the Maxwell model, according to which the elastic and viscous deformations are separate and do not affect each other. Its biggest limitations are that it shows unlimited deformation under constant stress and a level of irreversible deformation, which is not the case with viscoelastic materials. [33]

5.1.1 Shear Viscosity

During processing the most important rheological parameter is shear viscosity, also commonly merely referred as viscosity. Simplest way of examining shear viscosity is through simple shear flow, which means that the material is assumed to be placed between two plates. One plate stays in place, while the other is moved axially. The model is illustrated in Figure 5.2. Shear viscosity is the materials ability to withstand shear stress. When same stress is applied, with high viscosity material a little deformation is observed, and with low viscosity higher amount of deformation, respectively. [34]

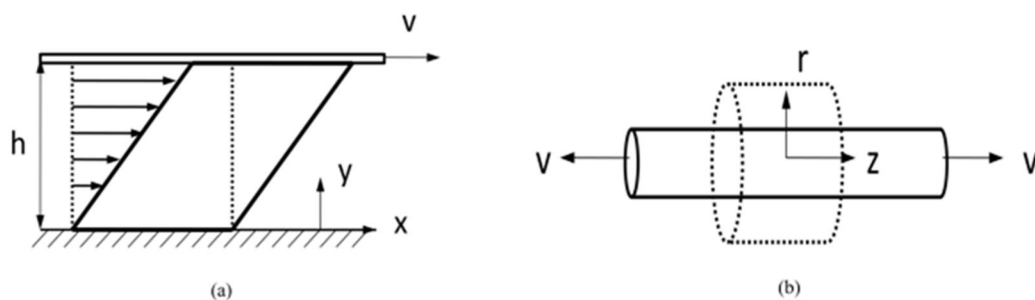


Figure 5.2. Illustration of simple shear flow (a) and uniaxial extension (b) [35].

Materials can be categorized by the way their shear viscosity changes when the shear rate is changed. Newtonian fluids, including water, have a constant shear viscosity. Materials with differing behaviours are called non-Newtonian fluids and consist of shear thinning and thickening. Polymers are shear thinning, which means that when the shear rate increases the shear viscosity decreases. Shear thickening fluids have increasing shear viscosity with increasing shear rate, respectively. Shear thinning is a common phenomenon, seen for example, in ketchup bottles, while shear thickening is rare. [34]

Viscosities can be measured with an in-line, on-line or an off-line rheometer. With in-line and on-line methods the measuring is done during processing. In an in-line rheometer measuring is done as material passes the sensor during processing, while in an on-line rheometer a side stream is separated from the actual flow and the sensor is used to analyse the side stream. An off-line rheometer is a specialized apparatus for measuring viscosities apart from the processing. Shear viscosity is usually measured with either of two off-line methods: capillary rheometer or rotational rheometer, shown in Figure 5.3. [36]

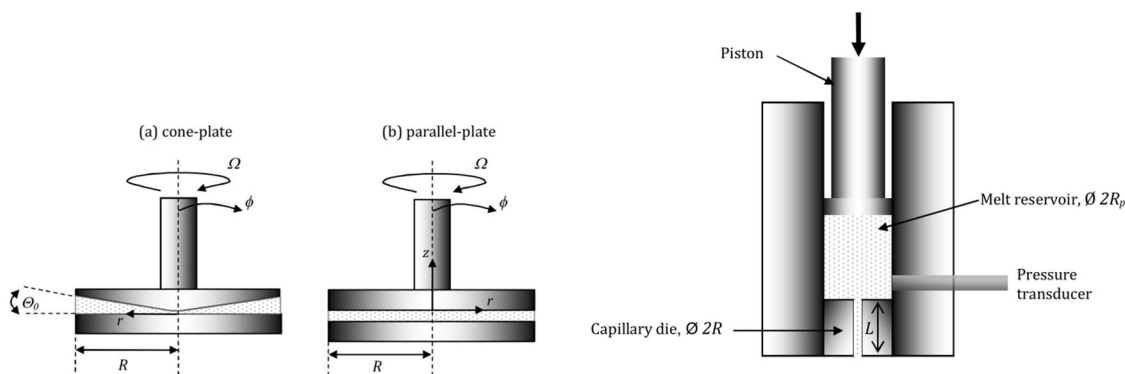


Figure 5.3. Cone-plate and plate-plate geometries for rotational rheometre (left) and capillary rheometer (right) [37].

In capillary rheometer the material is heated to a desired temperature in a cylinder and extruded through a capillary die. A sensor measures the pressure drop, which is the difference between the cylinder pressure and atmospheric pressure, and from that data shear viscosity is calculated. Rotational rheometer is based on two plates, one of which rotates around its axes creating a shear to the material. The shear viscosity is calculated from the information on how much stress was needed to achieve the wanted shear or

how much shear was needed to get the wanted stress. In addition to parallel plate geometry, a cone-plate or a concentric cylindrical geometry can be used. [37]

5.1.2 Extensional Viscosity and Melt Strength

When discussing foaming, extensional viscosity is a more important property. Extensional viscosity is the materials ability to withstand elongation, uniaxial, biaxial or planar. Uniaxial extension, and the deformation caused by it were illustrated in Figure 5.2. Melt strength is an engineering measure for extensional viscosity. It is the maximum stress that can be applied to the molten material without it breaking.

Like shear viscosity, extensional viscosity does not always remain constant with changing extension rate. Extension thickening, also referred as strain hardening, means that when the extension rate increases the extensional viscosity increases. Extension thinning means decrease in extensional viscosity, respectively. As all polymers are shear thinning, extensional properties depend on the material and its structure. As a generalization with polyolefins, linear structured materials such as linear low density polyethylene (PE-LLD), high density polyethylene (PE-HD) or PP are extension thinning, as branched such as low density polyethylene (PE-LD) are extension thickening. As PP is extension thinning, most of TPV materials are also. [38] With chemical treatment molecular structures can be modified from linear to branched. The same goes with SBS. It is extension thinning by nature, but can be temperature treated into extension thickening. [39]

When studying extensional viscosities, off-line methods can be used to create a shear-free load to the material, as on-line and in-line systems are always used to analyse mixed flows. One method for off-line rheometry is based on counter-rotating drums. Sample is attached to two drums, which start rotating elongating the sample at a constant rate. The method is based on simple extensional flow, which means shear free uniaxial flow, and the value for viscosity is calculated from the stresses used to achieve the wanted extension rate. One apparatus using this method is illustrated in Figure 5.4. [35, 37]

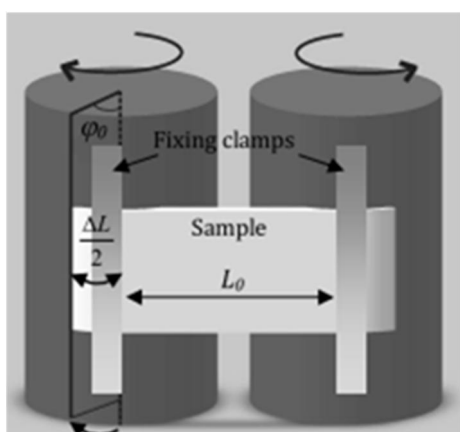


Figure 5.4. Counter-rotating drum device for measuring extensional viscosity [37].

As the foaming process consists of shear stress as well as extension, the mixed flow systems are considered to give more realistic results. The on-line and in-line rheometries are based on calculating viscosities from pressure drops inside the cylinder or die. The calculations and test setup for them are more difficult than with off-line rheometers, which is why the latter are used more often. For experimental part of this thesis, a rather easy way of estimating extensional viscosity from capillary rheometer data was used. It is discussed in more detail in Chapter 8.1.2. [35]

5.2 The Effect of BAs on Viscosity

Adding a notable amount of gas to a polymer matrix has to have an influence on material properties, and this is no different when considering rheological properties. It has been found that the addition of all BAs change the viscosity of materials. The shear and extensional viscosities both are affected.

The effect of BAs on **shear viscosity** has been researched fairly well. The degree of viscosity reduction does differ according to material and its structure, but the main lines seem to be coherent: increasing BA content lowers shear viscosity. In their research Qin et al. studied effects of different BAs on TPO. They found that PBAs had a bigger effect than CBAs, probably because CBAs have smaller gas content. Of PBAs the addition of CO₂ was found to have a greater effect on shear viscosity than N₂, owing to the different solubilities of the gases. Surprisingly it was found that N₂ releasing exothermic CBAs had a greater effect than CO₂ releasing endothermic CBAs. An example of a ratio between PBA concentration and relative shear viscosity of the solution is demonstrated in Figure 5.5. [35, 40]

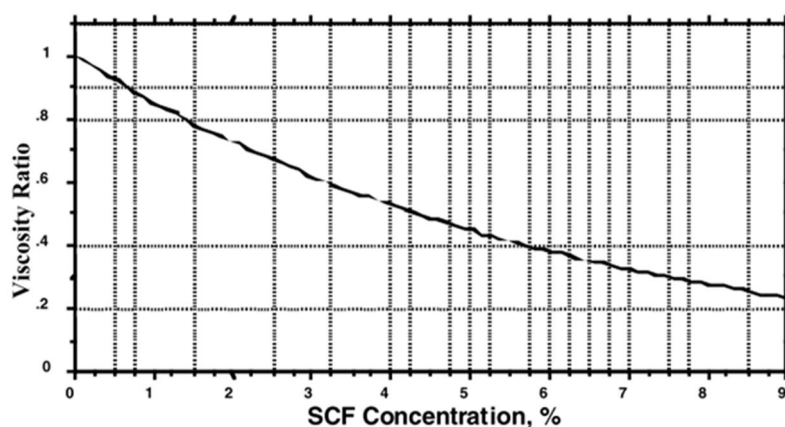


Figure 5.5. The correlation between SCF concentration and relative shear viscosity of a polymer material [21].

The reduction in shear viscosity enables use of lower pressures and clamp tonnage during processing. This reduced pressure leads to less internal stresses and thus less warpage. It is also possible to shorten the cycle time because the decreased pressure

allows elimination of pack and hold time and lower viscosity causes lower shear temperatures thus shortening cooling time. [32]

The effect on **extensional viscosity** has been studied far less than shear viscosity, which is mostly due to difficulties in measuring. With the technology today it is impossible to create a shear-free flow for materials saturated with gas. In order to maintain the desired saturation, temperature and pressure have to be strictly regulated. At the moment this is not possible with off-line rheometers, and the use of on- or in-line rheometers is more difficult, and the results still more debatable. The research on the subject has been done on few materials, including polybutylene succinate and PP, and it has been found that the extensional viscosity decreases with addition on a BA. [35]

As the interesting phenomenon in shear viscosity is observed during diffusing gas into the polymer, the interest in extensional viscosity peaks as the gas diffuses from the material into the nucleated cells. When BA diffuses out of the material, viscosity increases. This is partly because of the decrease in the BA concentration but also other factors play a part. As the phenomenon is more closely related to the cell growth process, it is further discussed in the next chapter. [35]

5.3 Effect of Rheological Characteristics on Cell Growth

During cell growth both shear and extensional viscosities are important, but the latter plays a bigger role. Cells grow by the force induced by gas diffusing into the cells. The pressure is balanced by melt pressure, which is mostly determined by shear viscosity. Therefore higher shear viscosity causes slower cell growth rates and smaller cells attributing to a more homogenous cell structures. At the same time as cells grow their walls elongate and become thinner. In order for the material to keep its integrity and not to rupture and collapse a high enough melt strength is needed. Both phenomena are illustrated in Figure 5.6. [40, 41]

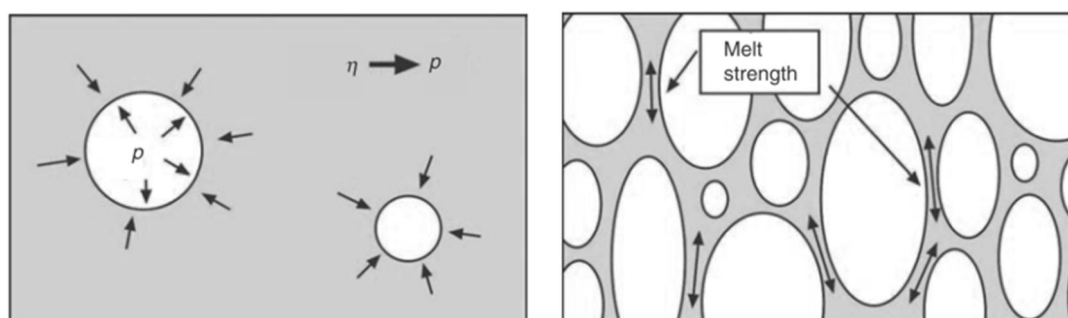


Figure 5.6. Forces influencing cell growth [41].

According to extensional viscosity foaming process can be compared to fibre drawing and film forming. They are all processes in which the molten material is drastically elongated. Fibre drawing is the simplest process because the material is only extended in one direction, while film forming induces biaxial or planar extension. In film extrusion the molten material is elongated in the die after which the film can be oriented by

pulling axially or biaxially. In film blowing the molten material is extruded through a small ring die and then blown thin. During blowing the material is elongated in all directions making film blowing the closest process to foaming. All these processes require good melt strength so that material does not fracture during quick extension. It has been noted that extension thinning materials can be rarely useful, since they rupture too easily as the extension rate increases. [37]

As has been mentioned before cells grow as long as viscosity of the material allows it, or until the walls collapse. During cell growth the gas diffuses into the cells, during which the BA concentration of the material decreases and the viscosity increases. Also contributing to the viscosity gain are the laws of thermodynamics. Diffusion of the gas, as well as the cell growth are both endothermic processes and induce cooling of the surrounding material thus raising viscosity. [35]

6 FOAMING OF THERMOPLASTIC ELASTOMERS

TPEs differ according to structure, and rheological and thermal properties, resulting that not all TPEs can be successfully foamed with all methods described in Chapter 4. Expanding microspheres require less from the foamed materials, so it can be used for almost all polymers. Also MuCell has been said to be usable for most polymers excluding liquid crystal polymers. [32] A lot of research has been done on the field of foaming TPEs, but only some material groups have gotten the interest of the academic community. Others have been studied for commercial purposes and the results have not been reported.

6.1 Styrenic Thermoplastic Elastomers

TPSs have been used as a material for shoe soles and in that application they also have been foamed. Unfortunately it is not one of the TPE groups which have been studied recently, and the information on foaming is scarce. SEBS can be foamed at least physically and with expandable microspheres.

Kropp et al. studied extrusion foaming of three TPEs, SEBS among them, with CO₂ as PBA. They were successful at foaming SEBS, but the cell structure was not homogeneous, with a solid edges and small celled inner regions. Also some crazing was observed. The achieved density was about 670 kg/m³ with the gas portion of 0.5 %. They believed that a better structure could be achieved by changing the die geometry.[42] It seems that in TPS's case usually expandable microspheres have been used in foaming. In a technical bulletin AkzoNobel states that Expancel microspheres can be used to foam at least SBS and SEBS of TPSs. A variety of different grades of SEBS have been foamed with expandable microspheres with a large variety of achieved cell structures. It was found out that the outcome of foaming is hard to predict as it depends on so many variables. [24]

6.2 Thermoplastic Rubber Vulcanizates

TPV is one of the TPE groups whose foaming has been under a lot of research. They can be foamed by chemical and physical foaming to have a wide variety of cell structures. They have also been successfully foamed using expandable microspheres. One of the most interesting aspects of TPV foaming is that water can be used as a foaming agent in physical foaming. This is a notable advancement since water is inexpensive, does not require special handling and is readily available. [23, 24]

In his research Sahnoune studied TPV foaming with water as a PBA. His study showed that it is possible to obtain low density foams with water, even though this had been questioned before. He studied foaming with water contents ranging from 0.6 to about 4 %, and the highest densities he achieved were 280-400 kg/m³ with 0.6 % water content. The lowest density he was able to achieve was 100 kg/m³ with 3.5 % water content. He found that increasing water content decreased the density, but only to about 3.5 % water content, after which the density started increasing. This was probably because at high concentrations the polymer becomes saturated and the BA does not distribute evenly, which leads to larger and ruptured cells.[23]

In the study by Kropp et al. discussed in previous chapter, also a PP/EPDM TPV material was tested. The used grade, especially developed for water foaming, proved most difficult to foam of the three test materials. The attained foam had a minimum density of 760 kg/m³ with a gas portion of 0.7 %. The cell structure was not homogeneous, presumably resulting from the high viscosity of the grade, and the cell size was bigger than with SEBS. [42] As Kropp et al. compared foaming of different materials with one PBA, Kim et al. compared different PBAs with one material. In their study they foamed a TPV with N₂, CO₂, n-butane and water. They found that smaller cell sizes could be achieved with N₂ and CO₂ than with n-butane and water. The former resulting in cell sizes ranging from 20 to 80 μm and the latter from 80 μm upward. N₂ was observed to give the finest and the most uniform cell structure with a smooth surface, proving that it can be successfully used to create TPV foams with higher densities. If lower density foams are preferred, CO₂ and n-butane are good candidates. It was also noted that as the BA content increased, cell sizes decreased. [7]

In a report by Trexel, Kent et al. discuss microfoaming for TPVs used as automotive weather seals. They conclude that numerous TPVs from different manufacturers have been successfully foamed with MuCell. Two tables from the report, one containing properties of various grades of foamed TPV and the other comparing properties of EPDM, microcellular TPV and TPV foams, can be found in Appendix 3. [38]

6.3 Olefinic Thermoplastic Elastomers

TPOs are mostly used in automotive industry, where their unique properties have led them to replace thermosets. Foaming TPOs would be an easy way of lowering material costs and fuel usage. Despite high demand TPO foams are not used in mainstream applications since their foaming method is still under development. One contributing factor to this is that TPO as a material is so complex that there is not sufficient knowledge of its properties to perfect the foaming. This does not mean that there is not literature covering TPO foaming. A lot of research has been done, and is being done at the moment, to perfect the foaming methods. So far TPOs have mostly been foamed on small scale during research. It has been found that they can be foamed physically, chemically and with expandable microspheres. Also a variety of different blowing agents have been used successfully. [8, 40]

In their research Maani et al. studied the difference of foaming linear (L-TPO) and branched TPOs (B-TPO). L-TPO like linear PP (L-PP) is extension thinning as their branched counterparts, B-TPO and branched PP (B-PP), are extension thickening. For PP it has been found that B-PP is more ideal for foaming as cell densities twice the amount of L-PP's can be achieved. In the study the opposite was observed: L-TPO was successfully foamed with cell density three times as big as the corresponding value for B-TPO. This was explained by the difference in the morphology in the un-foamed materials. The dispersed elastomer particles in L-TPO are smaller, resulting in a higher particle population, which means more nucleation surfaces, hence the higher cell density. [43] Kim et al. further studied the effect of elastomer particle size on cell size. For the study they used PP/ethylene-octene copolymer (EOC) blends with different morphologies. They were able to calculate an optimum domain size for EOC, 0.3 μm , with which the cell density could be maximized. [44]

6.4 Urethane Thermoplastic Elastomers

Because TPUs' disadvantages are mostly limited to hardness and cost, foaming could be an easy way of making the material more desirable. The only problem is that like with TPOs, TPUs do not still have a widely used foaming method. TPU is one of the groups under a lot of research. They have been successfully foamed by the means of physical and chemical foaming as well as with expandable microspheres.

As with SEBS, when foaming with expandable microspheres the outcome is hard to predict just by reading data sheets. It has been observed that amorphous TPU is quite easy to foam as the same for semi-crystalline TPU is difficult. The resulting foam densities are quite similar to the ones achieved by chemical foaming. [24] Nema et al. studied the effects of exo- and endothermic CBAs on TPU. They found that it was possible to achieve low density (787 kg/m^3) TPU foams with a blend of both CBAs. The resulting cell structure decreased the hardness from 85 ShA of the solid material to 55 ShA. [9]

The third material in the study of Kropp et al. was polyether-based TPU. Of all three it exhibited the best foamability with CO_2 as PBA. The minimum density was 400 kg/m^3 with 0.2 % gas content. The achieved cell structure was excellent and reduction in hardness was also observed. [42] Ito et al. studied the effect of saturation pressure and foaming temperature in cell morphology during foaming with supercritical CO_2 . They found that the gas is mainly present in the soft segment, resulting that mainly those areas exhibit cell nucleation and growth. As for the saturation pressure, they found that increasing pressure decreased the cell size, increasing the cell density respectively. [45] Champagne et al. have studied TPU foams for more exotic application, as cartilage replacement. In their study they foamed TPU with CO_2 solid-state batch process, and the resulting foams had microcellular structures and densities from 100 to 600 kg/m^3 . [46]

6.5 Copolyester Thermoplastic Elastomers

Compared to other materials discussed only little information has been found on TPC foaming. However it was found that in connection to the Dolphin method TPC has been physically foamed using MuCell. The grade used was Pibiflex® from P-Group, and it is said to be easily physically foamed. [47]

6.6 Thermoplastic Elastomers from Recycled Materials

TPEs from recycled materials can and have also been foamed. In a study Xin et al. introduced waste rubber tire powder into a PP matrix, and a small portion of pure SEBS was used as compatibilizer. The material was then microfoamed using a chemical foaming agent and injection moulded. With this process they were able to manufacture a cellular material with uniform microcellular structure with solid skin. They also noted that like with TPOs the elastomer particles act as nucleating surfaces and a higher amount results in higher cell density and smaller cell size. [48]

7 MANUFACTURE OF TEST PIECES

For the experimental part two materials were foamed with expandable microspheres. The materials were selected based on their previous performance as gaskets or promising test results. Expandable microspheres grades were selected for best performance with the materials. In addition to foamed samples, also solid reference samples were manufactured.

7.1 Materials

Materials selected for the thesis were two styrenic thermoplastic elastomers, more specifically SEBS. They will be referred as Material A (MatA) and Material B (MatB) in this thesis. One has been used successfully before and the other is a new blend with promising results from previous tests. Both materials have been blended to achieve high resistance to oil and fire, but differ in composition and price. A comparison of test materials is listed in Table 7.1.

Table 7.1. Comparison of test materials according to datasheets.

Material code	A	B
TPE type	SEBS	SEBS
Hardness (ShA)	62	60
Density (kg/m ³)	1390	1200
Compression set 22h, 70 °C (%)	-	43 (22h, 70 °C)
Flammability	V-0, 5VA (1.6 mm)	V-1 (1.5 mm)
Oil swell, IRM 903 (%)	+19.9 % (168h)	+24.5 % (70h)

As can be seen from the table, Material A has greater values for all listed properties. Flammability rating is greatly dependent on the thickness of test piece, but as the difference between thicknesses is only 0.1 mm, values are comparable. The same cannot be said about the oil swell values, as there is a 4 day difference between test times. But even though Material A was kept immersed more than twice the time as Material B, it still had lower volume change. There was no value given for compression set of Material A in datasheets.

7.2 Test Pieces

Manufacturing of test pieces was done in two locations: Expancel in Sundsvall, Sweden and Trelleborg in Sastamala, Finland. Test pieces done at Expancel were foamed with

expandable microspheres and the ones at Trelleborg were solid reference samples. Expanding microspheres were selected as a foaming method for this study because of the low investments needed for their use. Injection moulding was selected as a processing method, since it is the method used for the gaskets under observation.

7.2.1 Foamed

Foamed test pieces were injection moulded with expanding microspheres at Expancel. The plaques were the shape of a rectangle with walls of 150 and 100 mm and thickness of 5 mm. Two different grades of microspheres were used, both as a masterbatch with EVA as a carrier. The microspheres, referred as Expancel A (ExpA) and Expancel B (ExpB), were chosen by Lena Jönsson from Expancel as the best suitable spheres for the materials. Material A was first foamed with two microsphere concentrations, but the lower concentration was quickly left out. Materials and microspheres (MS) used for test pieces are listed in Table 7.2.

Table 7.2. Test pieces and their composition

Code of test piece	Material	MS grade	MS conc. (wt.-%)
MatA S1	A	A	1.55
MatA S2	A	A	3.25
MatA S3	A	B	3.25
MatB S2	B	A	3.25
MatB S3	B	B	3.25

As microspheres start expanding when they are injected, expansion is greatest in furthest places from the point of injection. The phenomenon causes density variation throughout the part, which is why it is important to take to account the place from which the samples are cut. Figure 7.1 illustrates foamed test pieces and samples cut from them. Point of injection is represented with a triangle in all illustrations. Sample places were picked to represent the whole test piece.

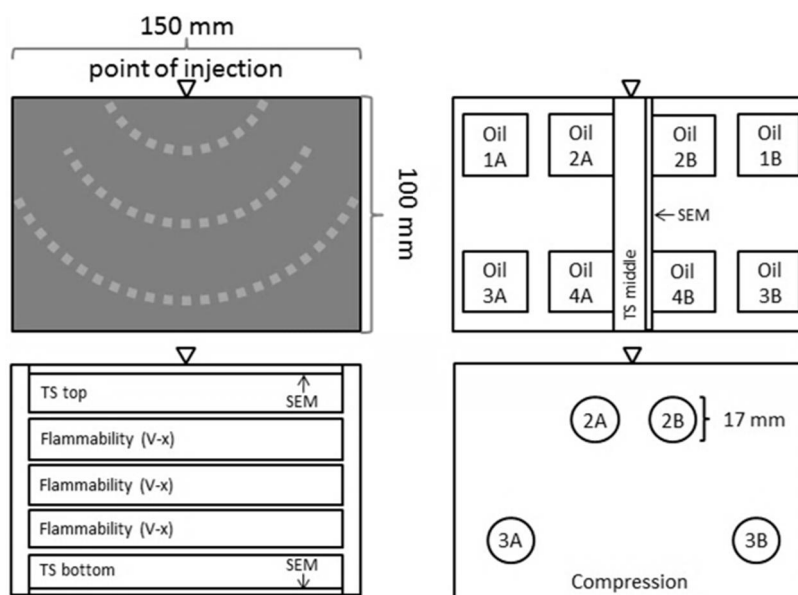


Figure 7.1. Illustration of test pieces done at Expancel and a sketch of samples cut from them.

It was assumed that if test pieces were cut vertically in half, the parts would be mirror images of each other. Therefore square and round samples with the same code number are considered parallel samples. For example 2A and 2B are parallel samples and averages were calculated from their values. Because the amount of test pieces was limited, parallel samples were limited to two.

7.2.2 Solid Reference Samples

Solid reference samples were manufactured at Trelleborg. There were five different shapes of plaques: two 25 by 25 mm squares with thicknesses of 1.5 and 3 mm, two 13 by 125 mm rectangles with thicknesses of 1.5 and 3 mm, and a multi-thickness plaque, with thicknesses of 2, 5 and 10 mm. The square pieces were used for oil resistance testing and the rectangles for fire resistance testing. Rest of the test samples were cut from multi-thickness plaques.

8 RHEOLOGICAL CHARACTERIZATION

Rheological testing was conducted to explain differences between the two materials in processing. Shear viscosity is the best property to predicted behaviour of expanding microspheres and was therefore measured. Extensional viscosity however dominates chemical and physical foaming and is relatively easy to evaluate from shear viscosity measurement data, so it was also calculated.

8.1 Method

The rheological measurements were done with a Göttfert Rheograph 6000 capillary rheometer using four different capillaries with L/D ratios of 5, 10, 20 and 30 and a temperature of 200 °C. The rheometer regulates the speed with which the polymer melt is extruded through the capillary die and measures pressure inside the cylinder or the die. Measurements were taken with six shear rates: 20, 40, 100, 200, 400 and 1000 1/s.

8.1.1 Shear Viscosity

To calculate shear properties, first the rate of extrusion needs to be known. Volume flow rate inside the cylinder (Q) can be calculated with equation

$$Q = \pi R_p^2 v_p, \quad (1)$$

where R_p is the cylinder radius and v_p is the piston speed. With Q apparent shear rate can be calculated using equation

$$\dot{\gamma}_{wa} = \frac{4Q}{\pi R^3}, \quad (2)$$

where R is the radius of the capillary die. The value is called apparent because an assumption of the flow needs to be done to use the equation. As viscoelastic materials do not comply with the assumption, a correction is needed. This is done by Schümmer approximation in eq. 6. [37]

Apparent shear stress can be calculated with equation

$$\tau_{wa} = \frac{\Delta p}{2L/R}, \quad (3)$$

where Δp is the pressure drop across the capillary, more specifically the difference between barrel pressure and atmospheric pressure, and L is the length of the capillary die. Again an assumption has to be made and a correction is needed. This is done by Bagley correction in eq. 5. [37]

From shear rate and shear stress a value for apparent shear viscosity can be calculated using equation

$$\eta_a = \frac{\tau_{wa}}{\dot{\gamma}_{wa}}. \quad (4)$$

As mentioned this is an apparent value as assumptions had to be made during calculations. As the tested materials do not comply with these assumptions, obtained values contain error. To get more realistic values corrections are made. [37]

Bagley correction takes into account that a level of pressure drop is experienced at the die entrance. The amount of entrance pressure drop (Δp_e) can be calculated using a series of capillaries with same diameter (D) and different length (L). A chart of pressure as a function of L/D - ratio is made and linear regression is used to determine the point of intersection with the pressure axis, which is the approximated value for Δp_e . An example of the method is shown in Figure 8.1. To calculate true shear stress, the value of Δp_e is subtracted from Δp , getting an equation

$$\tau_w = \frac{\Delta p - \Delta p_e}{2L/R}. \quad (5)$$

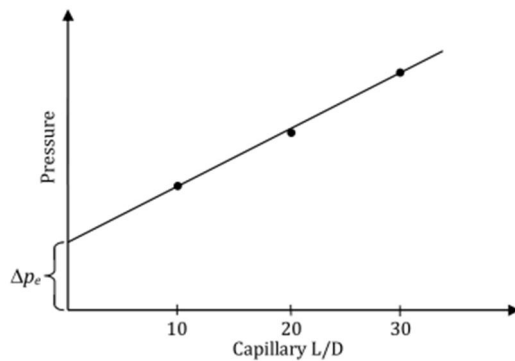


Figure 8.1. Determining entrance pressure drop according to Bagley correction [37].

When calculating shear rate more specifically shear rate at the capillary wall is calculated. When using equation 2 an assumption is made that the material is Newtonian and the shear profile thus parabolic. For shear thinning materials however the shear profile resembles a plug, illustrated in Figure 8.2. [37]

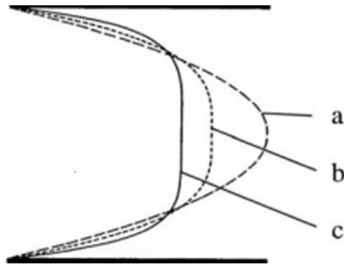


Figure 8.2. Shear profile for Newtonian (a) and shear thinning (b & c) materials [37].

Schümmer approximation is done by calculating the point where the true and Newtonian profile intersect, and using this point to calculate shear rate instead of the wall. The true shear rate is calculated by equation

$$\dot{\gamma}^* = x^* \dot{\gamma}_{wa}, \quad (6)$$

where x^* is a factor for shifting the distance. It can be calculated for capillary die with and equation

$$x^* = \left(\frac{3n+1}{4n} \right)^{n/(n-1)}, \quad (7)$$

where n is a Power-law index. However it has been proven that for most materials a value $x^* \approx 0.83$ can be used with good accuracy. Using the approximation shifts viscosity points only horizontally as for viscosity the x^* factor is cancelled out. [37]

8.1.2 Extensional Viscosity

For the thesis a method for calculating extensional from shear viscosity data was used. **The Cogswell approximation method** is based on the assumption that entrance pressure drop is partially caused by extensional viscosity. [49]

Extensional viscosity can be calculated from entrance pressure drop with a simple equation

$$\eta_e \approx \frac{\sigma}{\dot{\epsilon}} = \frac{(9/32)(n+1)^2 \Delta p_e^2}{\tau_{wa} \dot{\gamma}_{wa}}, \quad (8)$$

where σ is tension stress and $\dot{\epsilon}$ extension rate. Extensional stress can be calculated with equation

$$\sigma = \frac{3}{8} \Delta p_e (n + 1). \quad (9)$$

The method does not aim to give the true value for viscosity, but a good estimate, which is often enough, as was is in this case.

8.2 Results

Entrance pressure drop was determined for shear and extensional viscosity calculations. When comparing linear regression charts in Figure 8.3 the difference between materials is distinct. Values for Material A are over four times the values for Material B, which alone shows it has higher extensional viscosity and Bagley correction is needed.

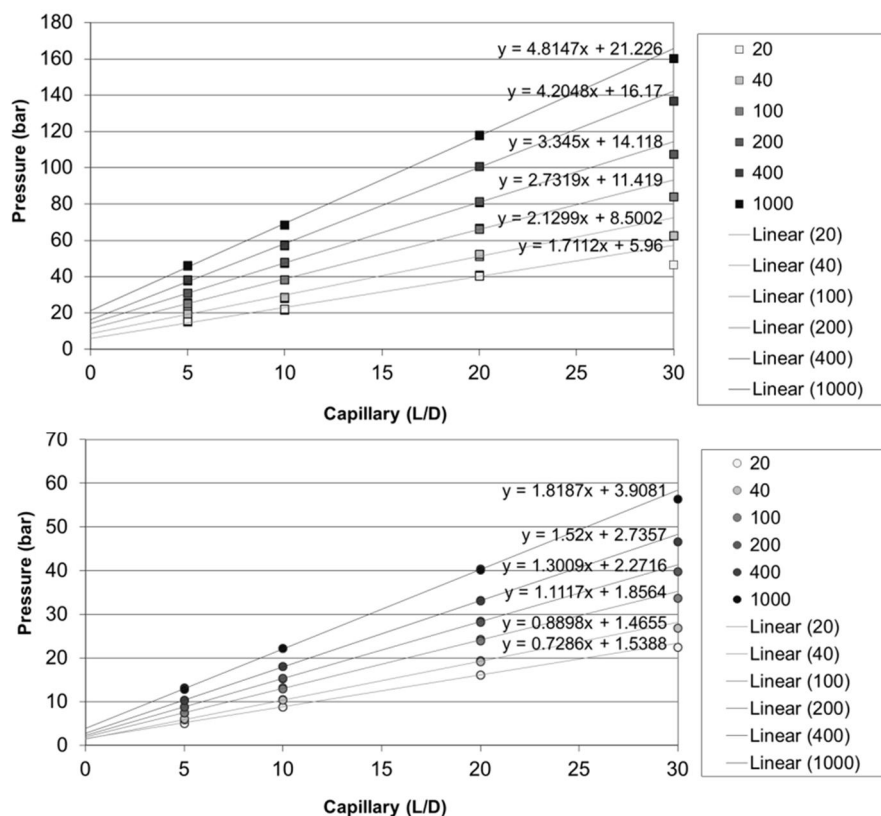


Figure 8.3. Determining entrance pressure drop for Material A (top) B (bottom).

When determining the entrance pressure drops, pressure values of all other capillaries seemed to align on the same trendline except for capillary 30/1, which showed lower values. Similar phenomenon, only the values for pressure with 30/1 capillary were higher than the line, was noticed by Aho [50]. She suggested that when using capillaries with high L/D ratio, pressure influences viscosity, causing error to measurements. The values obtained with the capillary were left out from the entrance pressure drop calculations, but were used in calculations later.

With entrance pressure drop values, Bagley correction was done. Schümmer approximation was then performed for these values. The difference between apparent and corrected shear viscosity values is shown in Figure 8.4. As they should, Bagley correction shifted values vertically and Schümmer approximation horizontally.

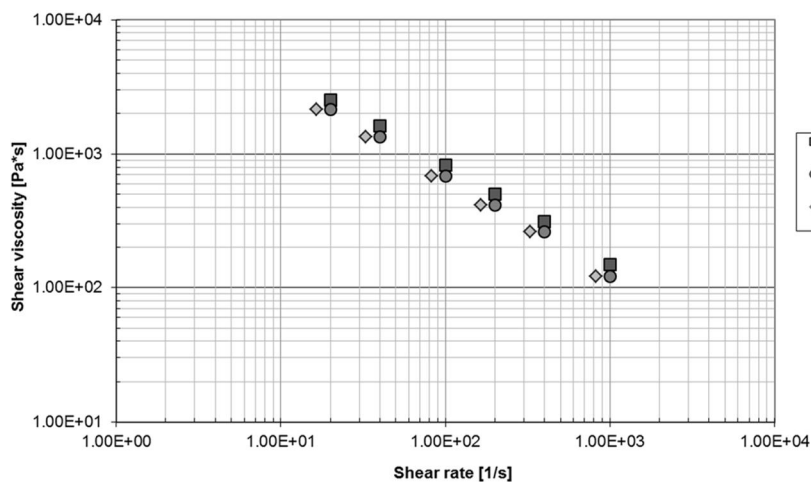


Figure 8.4. Apparent and corrected shear viscosity values for Material A with 20/1 capillary.

Results for shear and extensional viscosities are shown in Figure 8.5. Material A had distinctly higher shear viscosity than Material B, and for extensional viscosity the difference was even greater. This proves that even though they are the same TPE class, the materials have different characteristics and therefore different compositions.

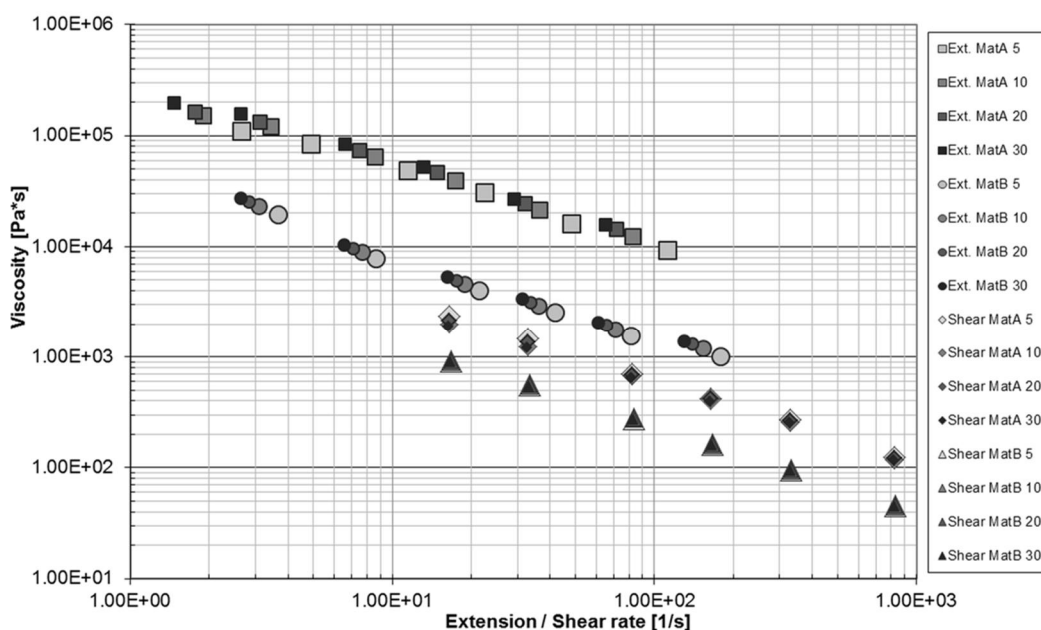


Figure 8.5. Shear and extensional viscosities of tested materials.

Jönsson stated that Material B was easier to foam with expandable microspheres which conforms to the lower shear viscosity. Material A on the other hand would, according to rheological testing, be more suitable for physical and chemical foaming, where higher extensional viscosity is needed. Also higher shear viscosity would, in theory, contribute to homogenous cell structure.

9 TESTING, RESULTS AND DISCUSSION

The motivation for this work was to find out if foaming is suitable method for gaskets to decrease hardness without affecting oil swelling, flammability, or compression properties. In addition density and tensile properties were measured. All tests were conducted on solid materials as well as foamed.

9.1 Appearance and Cell Structure

Appearance is not the most important property of gaskets, but as they are a visible part of a product, avoiding surface defects is desired. Cell structure is desired to be homogeneous so that cell sizes vary as little as possible and cell distribution is uniform throughout the part. As mentioned before, this is not possible with Expancel, as the density varies with distance to gate. However, if moulds are designed accordingly, the phenomenon can be used as an advantage.

9.1.1 Method

Appearance was evaluated by a visual examination. Cell structure was determined with Philips XL-30 scanning electron microscope (SEM) and stereomicroscope. In order to see the cell structure variation, fracture surfaces of three different places: top, middle and bottom, of one test piece were studied. The differences between test pieces were studied by comparing only “middle” samples. Figure 9.1 illustrates places of the fracture surfaces.

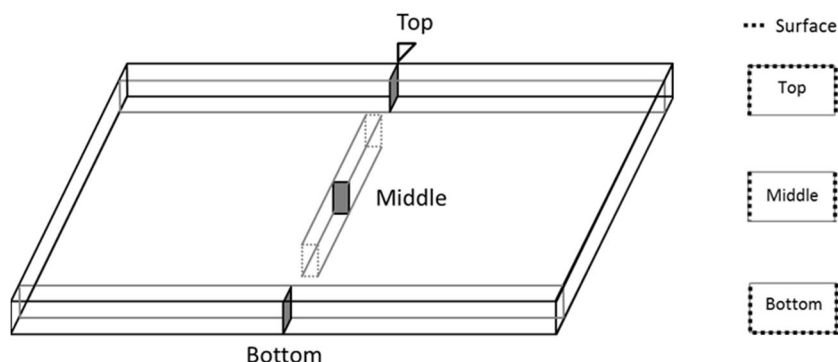


Figure 9.1. Illustration of the fracture planes on foamed test pieces.

Samples were cut so that in the top and bottom samples three, and in the middle sample two, of the faces were surface of the test piece. The fracture surfaces were achieved by first immersing cut sample in liquid nitrogen until it was completely frozen

and then hitting in the middle. In order to use SEM the samples also had to be gold coated.

9.1.2 Results

Visual examination showed silver streaks in all test samples. MatA S1 had clear streaks springing from the point of injection and perpendicular to the adjacent corners. MatA S2 and MatA S3 had clear streaks perpendicular to the point of injection. In Material B foams only slight silver streaks were seen and the shape resembled MatA S1. No other defects were noticed. Surfaces of foamed test pieces can be shown in Figure 9.2. Brightness and contrast of the pictures have been modified to show shapes better.

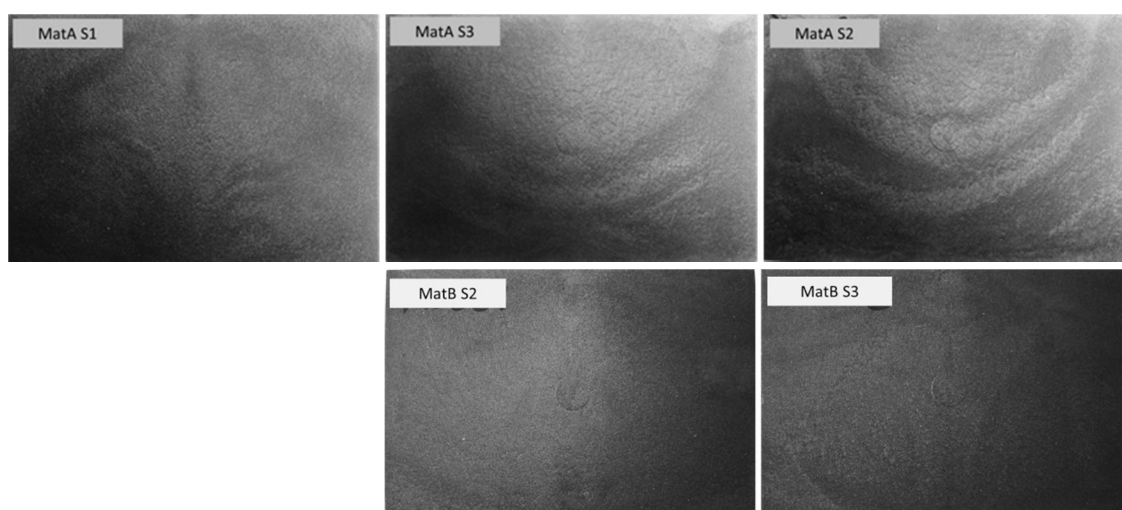


Figure 9.2. Surface of foamed test pieces.

The study of cell structure within a test piece was done for MatA S1. Pictures were taken with SEM and stereomicroscope. As no specific information on cell sizes was needed, stereomicroscope pictures proved to provide more information. In the “top” sample almost solid surface can be seen. Microspheres have not expanded in those areas, as pressure has been too high. Inside of the sample was full of cells with great variety of cell sizes, which is not desired. The “middle” sample had solid surface, but also flattened cells could be seen. This was due to expanded material hitting the surface of the mould and being pushed against the surface by pressure. Heterogeneous cell structure was again seen in the inside area. In the “bottom” sample the surface was not solid, but full of flattened cells. The inside was again full of spherical cells. The stereomicroscope pictures are shown in Figure 9.3.

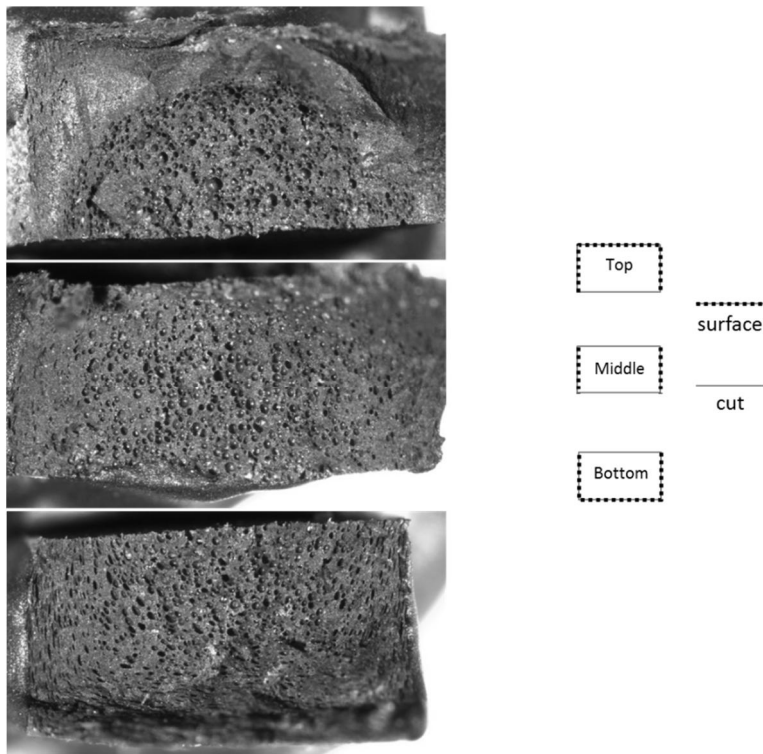


Figure 9.3. Stereomicroscope pictures of MatA S1 fracture surfaces: top, middle and bottom.

A comparison between test pieces was done from SEM pictures, in Figure 9.4. All samples showed spherical, closed cells with cell sizes varying from 20 to 150 μm . S2 and S3 for both materials showed similar structures. It was clearly seen that MatA S1, which had the lowest microsphere content, had the most heterogeneous cell structure. The other samples had higher concentrations, which had led to tighter and more homogeneous structure. As cell density was higher, spheres did not have as much room to expand, keeping the average cell size lower. Larger pictures are shown in Appendix 4.

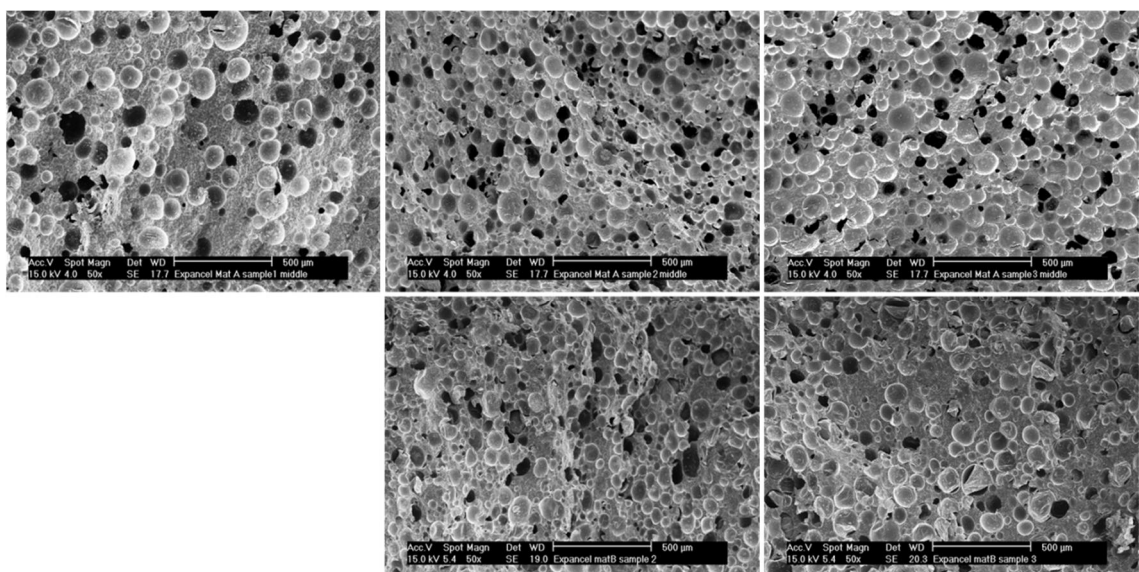


Figure 9.4. SEM pictures of foamed samples.

9.2 Density

Density is an important property when studying foamed materials. The relation between densities of solid and foamed materials represents the degree of foaming and usually the bigger the degree of foaming, the more other properties are affected. In this thesis the degree is presented as relative density, which is the density of the foam divided by density of the solid material. Another way is to subtract that value from 1, getting the amount of density loss.

9.2.1 Method

Density was measured during oil swell-testing. Density measurements were taken from eight parts of the foamed test piece, A and B being parallel samples. The illustration is shown in Figure 9.5.

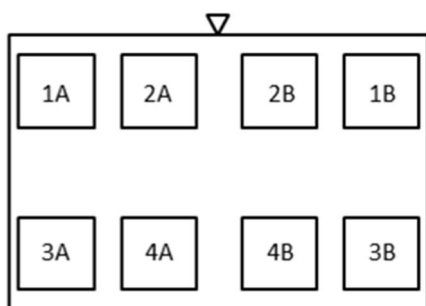


Figure 9.5. Illustration of density measurement samples in foamed test pieces.

Measurement was done by first measuring dimensions of a part with a micrometre screw gauge and then weighing the part in air. Density was then calculated by dividing the weight with volume. The value is an average of two parallel samples.

9.2.2 Results

Results of density measurements are shown in Figure 9.6. As was seen in datasheets, Material A had higher density than Material B. The measured densities also corresponded well to the given values. MatA S1 was the only foam to have 1.55 wt.-% microsphere content and had the highest density respectively. Only a small difference was seen between S2 and S3 for both materials, suggesting that the tested microspheres were similar.

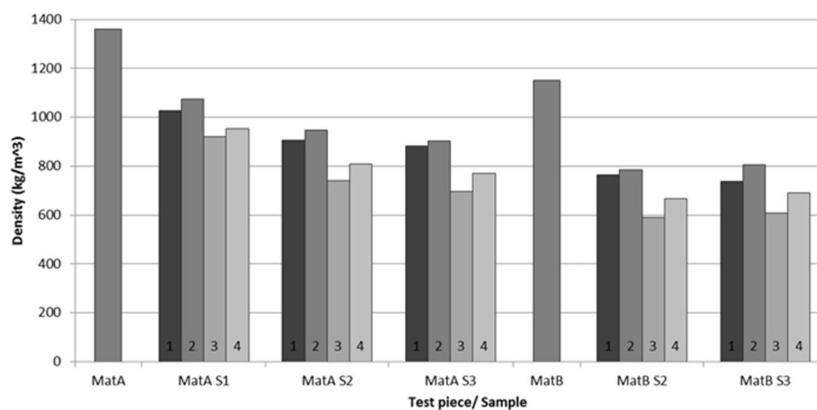


Figure 9.6. Density values of solid and foamed materials.

As was seen in Figure 9.5 order of samples from closest to furthest from injection point is 2, 1, 4, 3. The same order can be seen in densities. The sample closest to the point of injection had the highest density and as distance increased, density decreased. This was expected and corresponds to the melt pressure distribution inside a mould.

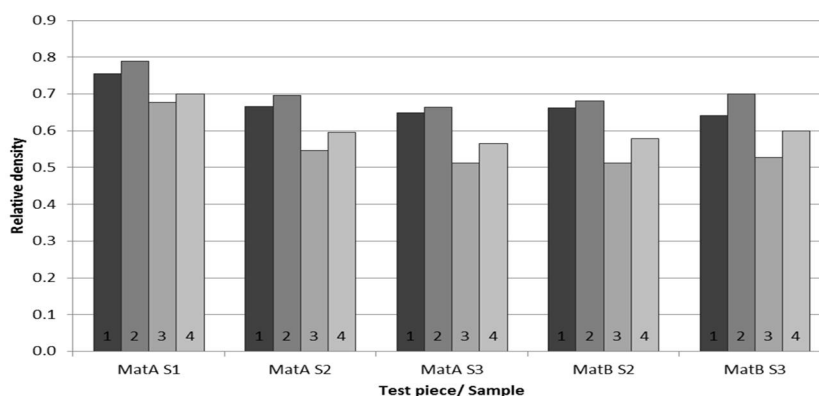


Figure 9.7. Relative density values of foamed materials.

Relative densities of foams are shown in Figure 9.7. It shows that the relative densities achieved with both microsphere grades are quite similar, only MatA S1 differs. Also the density gradients are alike. Differences between foams are minimal and can be explained by error in measurements.

9.3 Hardness

Hardness of the gaskets has to be low enough to allow easy installing. It is also imperative to the functionality of the gasket that the material has compressibility for tight sealing. The optimum value is regarded to being between 50 to 60 ShA, but also softer materials are desired.

9.3.1 Method

Hardness was measured according to standard UL 157 Gaskets and Seals [51]. Foamed samples were taken from the same points as density measurements, and points of density measurements were shown in Figure 9.5. Solid reference samples were tested with thickness of 5 mm, to ensure comparison.

Measurements were taken using a Shore A type durometre. Test piece was placed on a straight plate, durometre needle was pressed perpendicular to the sample and the metre was read within 1s, more precisely almost immediately after pressing. Two parallel measurements were taken and an average was calculated.

9.3.2 Results

Results of hardness measurements are shown in Figure 9.8. Measured values for solid materials were higher than the ones in datasheets. This was presumably because the standard gives a 1 second window for reading the value and in that time the value drops at rapid rate. To get comparable measurements the value was taken almost immediately, leaving the values higher.

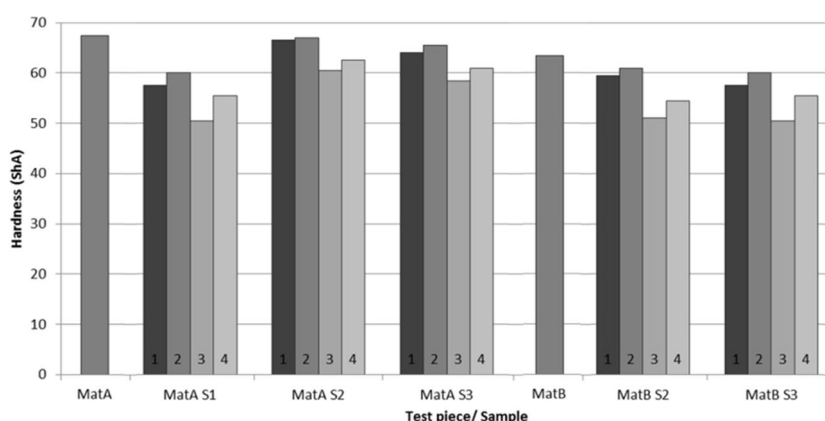


Figure 9.8. Hardness values of tested samples.

With S2 and S3 for both materials the highest hardness values did not differ a lot from the solid samples. This suggests that a great drop in density is needed to achieve a great drop in hardness. However, MatA S1 has lower hardness than other foams even though its density was higher. The difference is better seen in Figure 9.9, which shows density dependency of the hardness values.

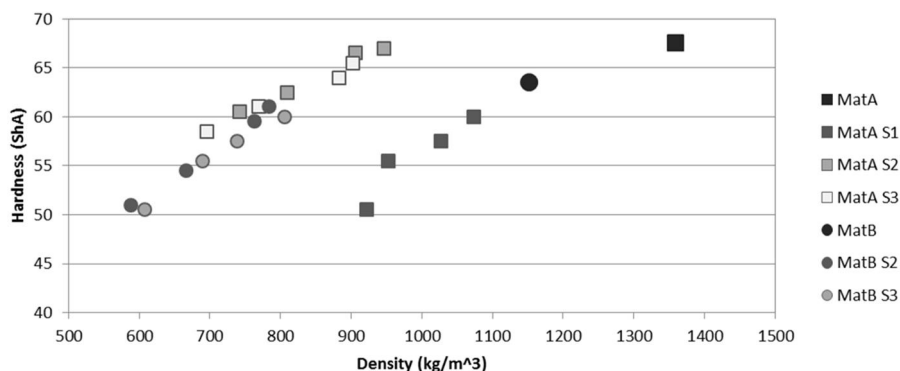


Figure 9.9. Density dependency of hardness.

The figure shows that S2 and S3 all follow the same trend. Also MatA S1 follows a similar trend, but with lower values. It can be speculated that hardness is dependent on cell sizes or cell density as well as relative density. It was seen in Chapter 9.1.2 that MatA S1 had less but larger cells contributing to larger defects and thus lower hardness. Solid materials seem to align with MatA S1, which indicates that small cells might actually harden the material to a certain degree. However more study would be needed to draw definite conclusions.

9.4 Tensile Properties

Tensile properties play a role during installation, as gaskets have to be easily stretched without them breaking. It is also hoped for that the gaskets stay intact during removal. As gasket elongations a material has to endure are in the range of 5-20 %. Tensile testing is also used as a method for quality control of materials and processes. If tensile properties differ, something is amiss.

9.4.1 Method

Tensile strength and elongation were measured according to standard UL 157 Gaskets and Seals [51]. Foamed materials were tested as rectangle samples cut from test pieces. To study the differences within a test piece, horizontal samples were taken from the top (T) and bottom (B), and a vertical sample was taken from the middle (M). The top and bottom samples were cut so that edges of the test piece were cut out. An illustration of the samples is shown in Figure 9.10. Solid samples were dumbbells, in accordance with the standard.

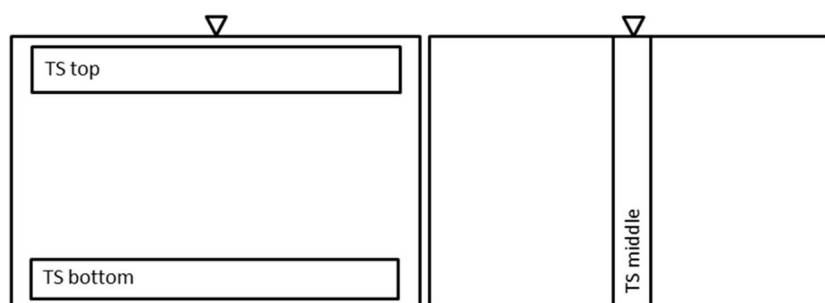


Figure 9.10. Illustration of the foamed samples used in tensile testing.

Measurements were taken with Messphysik midi 10-20/4x11-instrument equipped with a long travel extensometer. Samples were the shape of a rectangle or dumbbell having a straight section of 25 mm for measuring elongation. Samples were preconditioned for minimum of 30 minutes in 23.0 ± 2 °C and 50 ± 5 RH. Draw rate was 500 mm/min and elongation was determined with an extensometer. 20 % modulus was calculated.

9.4.2 Results

Results for 20 % modulus are shown in Figure 9.11. No uniformity was seen, as the modulus seemed to stay the same or increase for Material foams, but decrease for Material B. The differences between samples were even more diverse, as no test piece was alike. Only trend that can be seen in all but one test pieces is that value for Top sample was lower than value of Bottom sample. Also no density dependency could be distinguished which is better shown in Figure 9.12.

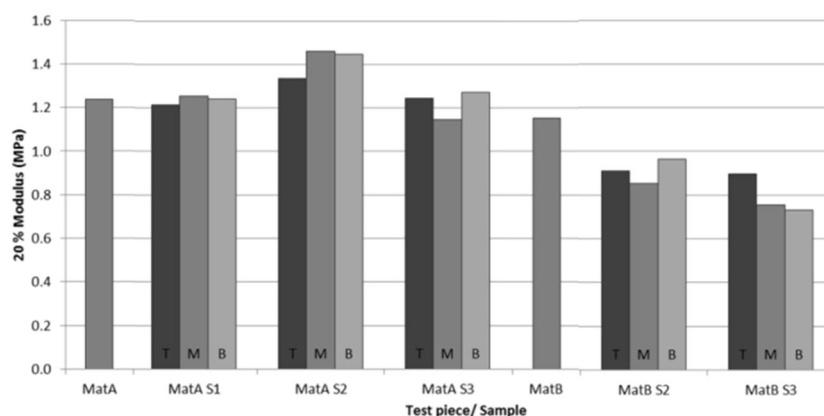


Figure 9.11. 20 % modulus values for tested materials.

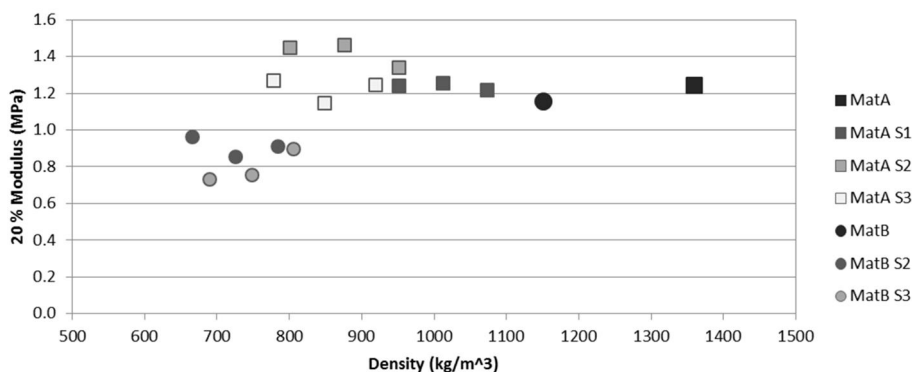


Figure 9.12. Density dependency of 20 % modulus.

Differences are easily seen in stress-strain curves, in Figure 9.13, where the curve for solid material is shown within curves of foamed samples. For MatA S1 curves seem to align on top of each other, which was also seen in modulus values. For MatA S2 and Mat S3 curves, except MatA S3 B, aligned similar to the solid curve, only higher. MatA S3 B on the other hand seemed to dive at first, but rose to almost the same stress levels as the other ones near 20 %. Foams of MatB had similar values with MatA at low strains, but started to diverge between 5 and 10 % strain, causing stress levels to stay well under the values of solid material. Larger images can be found in Appendix 5.

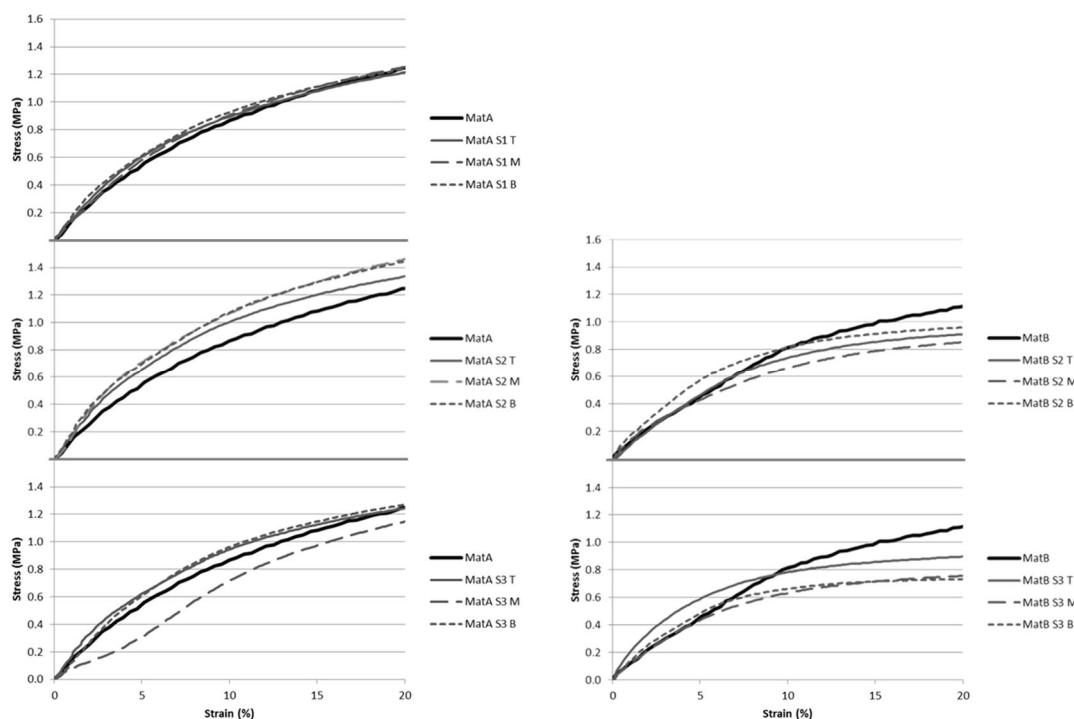


Figure 9.13. Stress-strain curves for the tested materials.

No distinction to how foaming affects tensile properties at low strain rates could be made. If gaskets were foamed, the suitable tensile properties should be determined to ease material selection. The achieved degree of change in tensile properties might be so low that no difference would be seen in the real use of gaskets.

9.5 Compression Properties

Compression set is an important property for functionality of the material as a gasket. Compression set represents the materials ability to withstand creep, and therefore maintain the ability to seal, under compression. For material to work properly as a gasket, it should have compression set of 20 % or lower. Compression deflection, meaning the force that is needed to achieve a certain deflection, was measured as parallel value to hardness to represent sealability.

9.5.1 Method

Compression set testing was done according to standard UL 157 Gaskets and Seals, excepting the sample sizes [51]. Samples were cut from the point of highest and lowest density of the test piece. Illustration of foamed samples cut for compression set is shown in Figure 9.14. According to the standard samples should be round with a diameter of 28 mm and thickness of 12.5 mm. Foamed samples cannot be stacked to achieve the thickness. As the test pieces were 5 mm thick, the requirement was not met. To achieve a value that could be at least remotely compared to previous results, diameter of the samples was reduced to 17 mm, bringing thickness/diameter ratio closer to the one used in the standard.

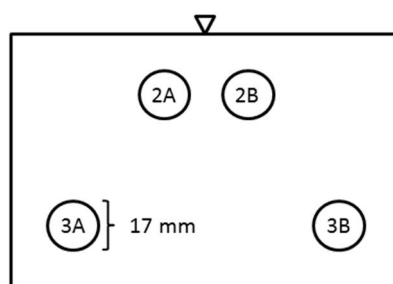


Figure 9.14. Illustration of the foamed samples used in compression testing.

In compression set, thickness of samples was first measured. Samples were placed between two plates, which were then docked and brought to a desired distance with screws. The rack was moved to a space with a desired temperature and left for 22 h. For foamed materials the temperature was 23 °C, and for solids 70 °C. After the time had passed samples were taken out and left to recover in 23 °C for desired time, after which their thickness was again measured. The recovery time for foamed materials was 24 h, and for solids 30 min. For comparison, solid samples were also tested with “foam conditions”. Values for compression set were then calculated from difference in thicknesses before, during and after compression.

Compression deflection was done according to standard ASTM D1056-00 Standard Specification for Flexible Cellular Materials—Sponge or Expanded Rubber [52]. Same samples were used for compression deflection as for compression set. Measurements were taken with Messphysik midi 10-20/4x11-instrument. A sample was com-

pressed between two plates with a speed of 50 mm/min to a 50 % deflection and corresponding stress was calculated.

9.5.2 Results

Compression set results with “solid conditions” are 65 % for MatA and 35 % for MatB. As the given value for MatB was 43 %, results can be considered approximates. A value for MatA was not given in datasheets, but the results show that it clearly has a greater compression set. Results for the “foam conditions” are shown in Figure 9.15. Values for solid materials are close and do not show the same amount of difference as the “solid conditions” did. However Mat B still has a lower value.

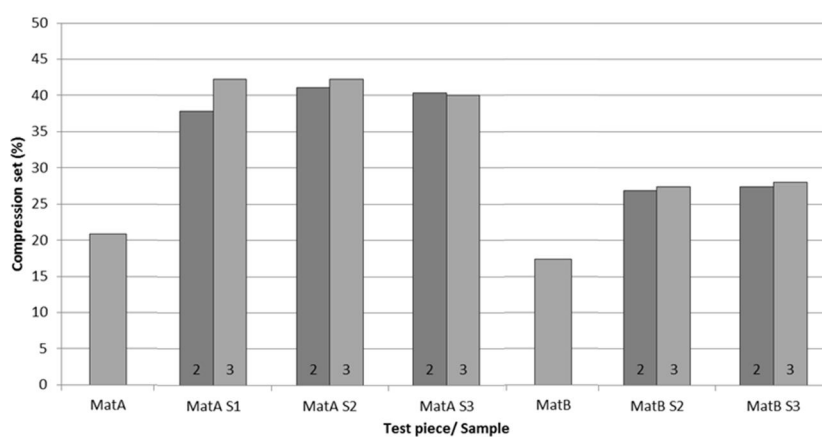


Figure 9.15. Compression set values for tested materials.

All foams have high values compared to solids and only small differences, which can be explained by error, can be seen between test pieces or samples of the same material. This suggests that compression set is increased by foaming but it is not dependent on density of cell size. Density dependency is better shown in Figure 9.16. It can be clearly seen that no dependency exists.

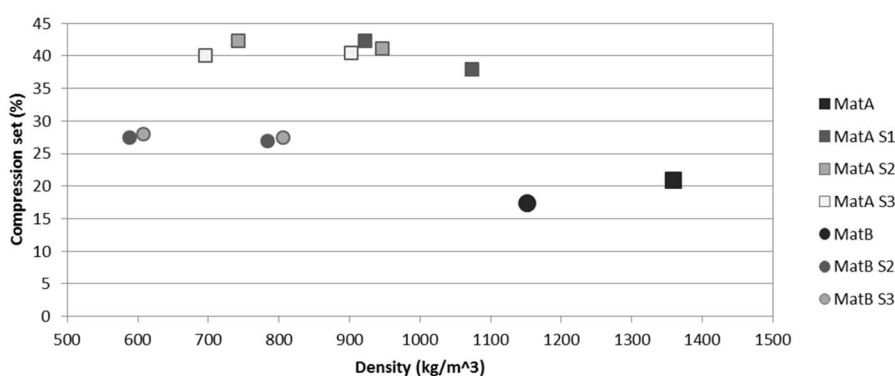


Figure 9.16. Density dependency of compression set.

Compression deflection results are shown in Figure 9.17. What is first noticed is that values do not seem to comply with compression set values, suggesting that the two

compression properties are dependent on different variables. This is quite possible as compression deflection measures the materials ability to withstand compression and compression set materials ability to recover from it. Compression deflection can be more precisely compared to hardness.

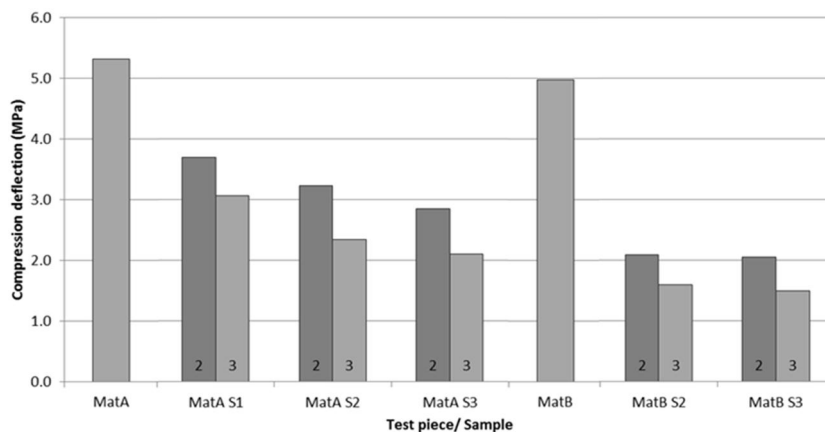


Figure 9.17. Compression deflection values for tested materials.

For solid materials the difference in stress is quite small, but for foams it is very distinct. For MatA foams, there is a clear difference between test pieces and samples within test pieces. For MatB foams the difference is not as clear between test pieces, but samples exhibit the same behaviour as MatA foams. This suggests that compression deflection is dependent on density. The phenomenon is better shown in Figure 9.18, where the dependency can be clearly seen.

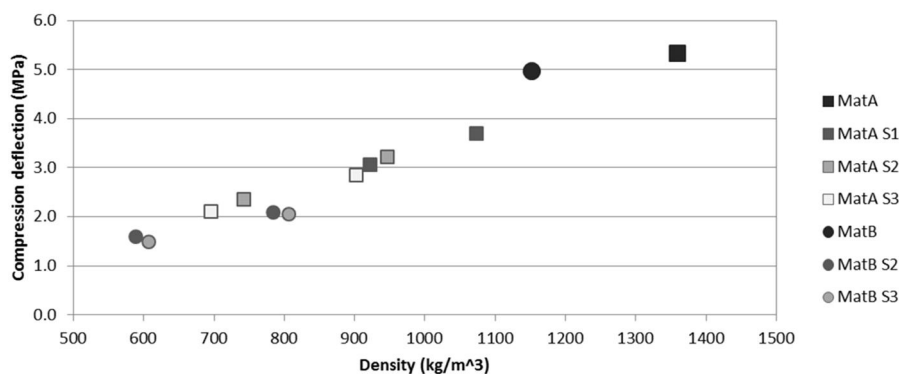


Figure 9.18. Density dependency of compression deflection.

All samples for MatA seem to align on a same line. Foamed samples of MatB seem to align a little lower than MatA, but the solid sample clearly higher, suggesting that either there is error in the value of the solid sample or MatB is more affected by foaming.

9.6 Flammability

Gaskets rarely come into straight contact with fire, but it is a possibility and has to be taken into account. Flammability ratings are also required for ingress protection ratings for the frequency converter casings.

9.6.1 Method

Flammability was measured according to standard UL 94 Test for Flammability of Plastic Materials for Parts in Devices and Appliances [53]. A 20 mm Vertical Burning Test, V-0, V-1 or V-2, was conducted. According to the standard samples are to be 125 by 13 mm rectangles with a maximum thickness of 13 mm. Foamed samples were cut horizontally from the middle of the test piece, illustrated in Figure 9.19, leading to different densities in samples. The place they were cut was noted. The reference samples were the rectangles injection moulded to meet requirements of the standard, with thicknesses of 1.5 and 3 mm.

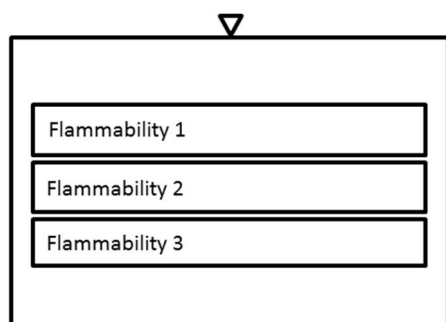


Figure 9.19. Illustration of the foamed samples used in flammability testing.

For testing sets of three parallel samples were used. Samples were pre-conditioned at 23 °C and 50 RH for 48 h prior to testing. During testing sample was exposed to a flame, with cotton ball underneath, for 10 s. after which it was taken out and time of afterflame (t_1) was measured. Right after the afterflame ceased the sample was again exposed to flame for 10 s. Time of afterflame (t_2) and afterglow (t_3) were recorded. Flammability rating was determined from the measured times and whether burning drops had set the cotton ball on fire.

9.6.2 Results

As the samples were only conditioned in room temperature, values are not fully comparable with the official flammability ratings. From tests for the thesis all test pieces, foamed and solid, got the highest, V-0 rating which was not expected as Material B has a lower rating, and foaming was expected to increase flammability further. Because all samples got the same rating, results have to be compared by the test criteria. A summary of test records is shown in Table 9.1. According to UL 94 ratings are given by 5 criteria. In order to get a rating sets of five samples, preconditioned in 23 °C and 70 °C, are test-

ed and all have to meet the requirements. There are criteria for individual specimens as well as for the whole set. The summary table only shows maximum values and the most radical behaviour. All test results can be found in a more detailed table in Appendix 6.

Table 9.1. Summary of flammability results according to UL 94 criteria.

	Thickness (mm)	C1, max (s)	C2, max (s)	C3, max (s)	C4, max	C5, max
MatA	3	0	0	0	No	No
MatA S1	5	0	0	2	No	No
MatA S2	5	0	0	0	No	No
MatA S3	5	0	0	2	No	No
MatB	3	1	2	6	No	No
MatB S2	5	5	15	5	No	No
MatB S3	5	4	13	4	No	No

Cx = Criteria for classification [53]
 C1: Afterflame for each individual specimen (t1 or t2). Maximum value of all tested specimen.
 C2: Total afterflame time for any set ($\sum t_1+t_2$). Total sum, calculated to match a set of five specimens.
 C3: Afterflame and glow after 2nd burn for individual specimen (t2+t3). Max. value of all specimens.
 C4: Afterflame or glow for any specimen up to the holding clam. Most radical behaviour.
 C5: Cotton indicator ignited by flaming particles or drops. Most radical behaviour.

Solid and foamed samples had different thicknesses resulting in un-comparable values. Thicker samples get lower flammability results as there is more material to burn. However as foamed samples had a greater thickness but still resulted in higher values, it can be reliably said that foaming increases flammability.

Material A had noticeably lower afterflame and afterglow times. In fact no afterflame was seen during testing. Also no afterglow was seen in solid samples, but in foamed samples a few seconds afterglow was noticed proving that flammability indeed had increased. For Material B the differences were clearer. None of the samples showed afterflame after the first burn, but for all foamed and one solid sample, it was seen after the second burn for several seconds. Afterglow was not noticed on any foamed samples, only on one solid sample.

As a summary it can be said that foaming increased flammability for both materials. Material A seemed to be influenced less as it has lower flammability. No clear degree of property loss could be calculated as the samples were not comparable. In order to make reliable conclusions further study is needed with same thickness samples.

9.7 Oil Swell

Oil swelling is as flammability, usually required for product approval. Furthermore the swelling plays a great role in the functionality of the gasket, if it comes into contact with

oil. A gasket that has swollen, is not the right size for the application, and may not work properly, or may not be easily reinstalled if it is removed.

9.7.1 Method

Oil swell tests were done according the immersion test –procedure in standard UL 157 Gaskets and Seals [51]. The test is supposed to be done for samples with the actual gasket thickness, but as the gaskets in question have complex geometries, this would be hard. In her thesis Miettinen found that 3 mm thick 1” by 1” (25.4 mm by 25.4 mm) square test pieces best represented the actual gaskets [5].

The oil swell testing was done for the same foamed samples as the density and hardness tests. Illustration is shown in Figure 9.20. Reference testing was first done with 5 mm thick cut samples to comply with the foamed samples. In previous testing it has been found that the thickness and whether the sample has been injection moulded or cut greatly effects results.

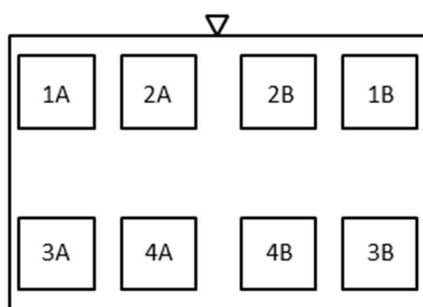


Figure 9.20. Illustration of the foamed samples used in oil swell testing.

According the standard first metal wire hooks are attached to samples, after which they are weighed in air and then in water. Before weighing in water the sample is first rinsed with alcohol and water. If the material is cellular, dimensions of the sample are measured with a micrometre screw gauge. Samples are then immersed in ASTM reference oil IRM 903 for 70 h, after which they are first dried with paper and weighed in air within 30 s., and then rinsed with alcohol and water before weighing in water within 60 s. of removing from oil. Again for cellular materials the weighing is replaced by measuring with a micrometre screw gauge. Volume change is then calculated from the values. According to the standard volume increase of 25 % or less is acceptable.

9.7.2 Results

Results for oil swell tests are shown in Figure 9.21. It can be clearly seen that foaming does not increase oil swell, but rather decreases it. This can be explained by oil penetrating and filling cells instead of polymer structure. Results for samples differ greatly between test pieces, suggesting error in measuring. No density dependency can be seen in oil swell. The dependency is better shown in Figure 9.22.

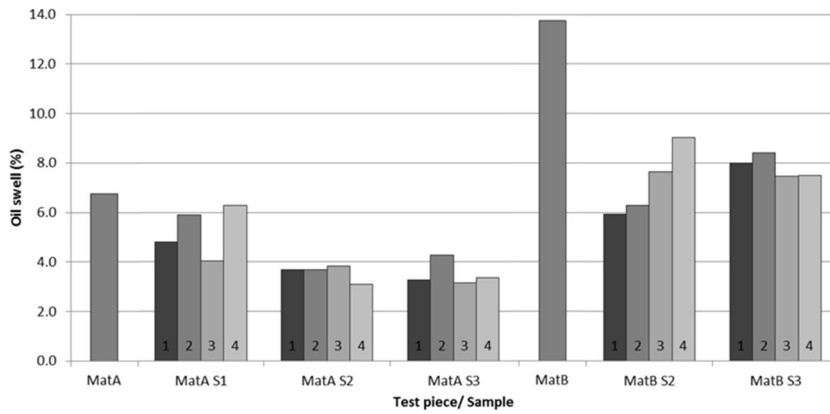


Figure 9.21. Oil swell values for tested materials.

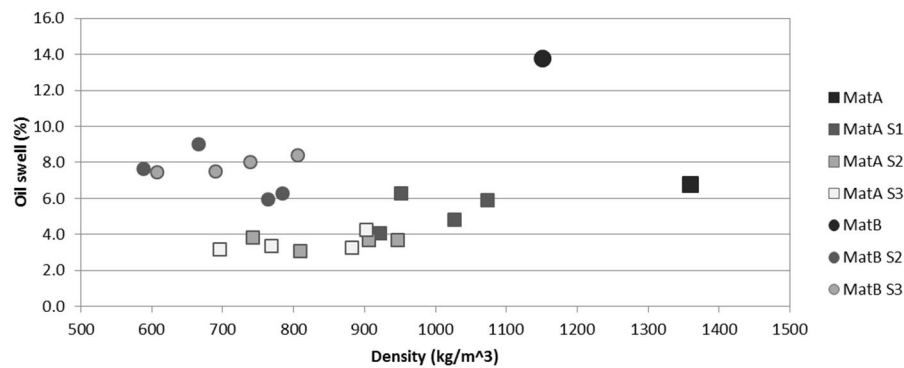


Figure 9.22. Density dependency of oil swell.

To ensure that differences in oil swell are indeed the result of measuring error weight change of the samples was calculated. The results, shown in Figure 9.23, proved to be interesting, as the differences between samples are quite similar, but do not follow the density order. As the density order from lowest to highest was: 2, 1, 4, 3, the weight change order from low to high was 1, 2, 4, 3. Also the differences between samples were great for MatB but quite small for MatA. The density dependency is better shown in Figure 9.24.

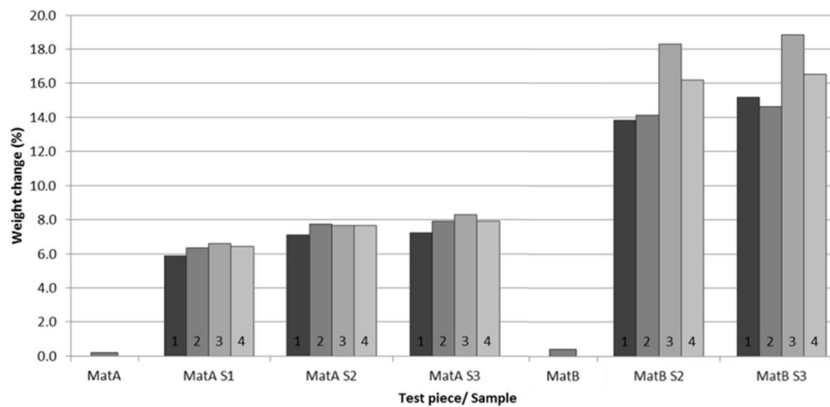


Figure 9.23. Weight change during oil swell testing.

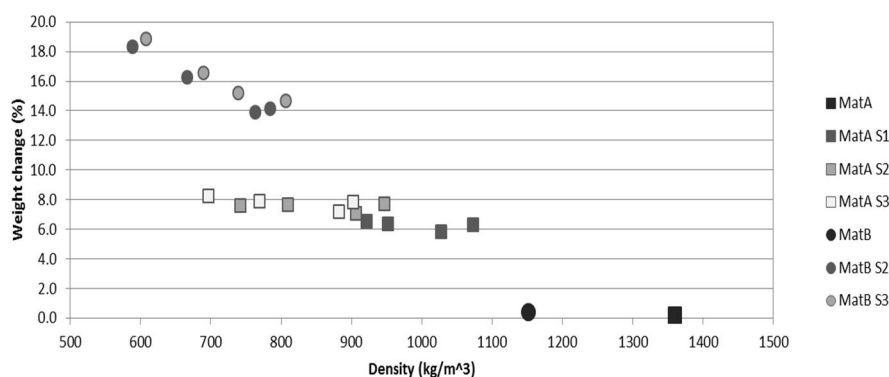


Figure 9.24. Density dependency of weight change.

Values for foamed MatB samples align on similar lines, weight change decreasing as density increases, excepting one sample for both foams. MatA foams align on a horizontal line, but a slight slope can be seen. The differences, however, are so small that they can also be caused by error.

Weight change seems to be dependent on density, but materials had clearly different behaviours, as one had a noticeable dependency and the other almost none. The differences in weight change between samples, more precisely why sample 1 with lower density, experienced a smaller weight change than sample 2 with higher density, could not be explained. It can be concluded that foaming does not increase oil swell, proving that foaming might be a viable method of improving gaskets.

10 CONCLUSIONS

Thermoplastic elastomers are a unique group of materials combining mechanical properties of elastomers and easy processability of thermoplastics. They offer a possibility to a wide range of new or improved applications. When replacing elastomers, they bring recyclability and savings in manufacturing process, when thermoplastics they offer improved impact resistance.

The objective of this thesis was to find out whether foaming could be implemented on gasket materials to offer new property-combinations. However, before foaming can be done, a material needs to be selected. Out of thermoplastic elastomer types that have been proven foamable, a few possibilities were selected. These included SEBS out of styrenic thermoplastic elastomers, thermoplastic rubber vulcanizates, urethane thermoplastic elastomers and copolyester thermoplastic elastomers.

There are three viable foaming methods that could be considered when foaming thermoplastic elastomers: physical, chemical and syntactic foaming, which all have their advantages. Physical foaming, which means dissolving gas or liquid to a material and initiating foaming through a change temperature and pressure, is a widely used method for manufacturing foams of all densities. Environmentally safe and cheap foaming agents, such as CO₂, N₂ and water can and have been used to foam a great variety of thermoplastic elastomers. However, high machinery investments are required to use the technology. Chemical foaming, meaning introducing gas forming chemicals into a material, on the other hand requires little or no machinery investments, but the chemicals cost more than gas and often cause discoloration in the product. Both methods also have high rheological demands for the matrix, as it has to have good melt strength to allow foam formation and high enough shear viscosity to form a homogenous cell structure. Syntactic foaming is less demanding, as it means introducing gas filled spheres into a material. Matrix material only has to have low enough shear viscosity to allow the expansion to happen. Syntactic foaming is also quite cheap to implement, as it requires little investment on machinery, but the savings are lost in material cost in the long run.

The experimental work was done with two grades of SEBS foamed with two grades of expandable microspheres. The SEBS grades were both blended for high oil resistance and low flammability. Expandable microspheres are a method of syntactic foaming. The microspheres consist of a copolymer shell and encapsulated hydrocarbon as a blowing agent. When spheres are heated during processing, blowing agent gasifies and its volume increases, causing the softened polymer sphere to expand. Expandable microspheres were selected for the thesis because of their easy use and low trial cost.

Two different microsphere contents were used and the achieved cell structures were varying, but rather homogenous. An unexpanded surface could be seen close to the in-

jection point, but at the further regions the surface consisted merely of flattened cells. The insides were full of cells, with varying sizes. Bigger cells were seen on samples with smaller microsphere content, as spheres had more room to expand. A difference was also seen on the surface as the two contents resulted in different shape silver streaks. Similar defects have been seen on solid and foamed TPEs in former studies.

The effects of foaming on several properties, important to gasket materials, were tested. Density is the most important property of foams, as it tells the degree of foaming. Samples with relative densities ranging from 0.5 to 0.8 were achieved. The largest difference within a test piece was over 0.15. All material/sphere combinations with the same sphere content seemed to result in similar density profiles. Hardness was clearly dependent on density, but not in comparison with the solid. For foams with higher cell density and smaller cell sizes relative hardness was increased. Previous studies show that a bigger drop in hardness can be achieved by chemical foaming. Whether high hardness is the result of a close and tight packed cell structure or presence of EVA stays a question.

An important property for gaskets is compression set, as it represents materials ability to withstand creep under compression. Foaming increased compression set clearly by almost doubling the values. Microsphere content or grade did not seem to play any role, as all foams of the same material had similar values. Compression deflection on the other hand was highly dependent on density and was therefore more comparable with hardness. Tensile properties were affected only a little by foaming and the results would indicate 20 % modulus increased for one material and decreased for the other. However the differences were mostly small, and would probably not affect the use of gaskets.

Flammability and oil swell were expected to increase by foaming, and flammability did. The two materials both had good fire resistance-ratings, and the one that had better seemed to be less affected. However testing was done with different thickness samples, and a degree of property loss could not be measured. Oil swell unexpectedly decreased as the permeated oil filled cells and not the polymer structure. Weight change was also measured to prove that more oil had indeed permeated the structure, even though the change in volume was quite small.

A rheological comparison between materials was performed. Shear properties as well as extensional properties were evaluated. A clear difference between materials was seen in both deformations. One material would, in theory be better suited for syntactic foaming, and the other for chemical and physical foaming.

As hardness and oil swell were both reduced and only compression set seemed to be drastically affected, it can be concluded that foaming might indeed be a possible way of improving gasket materials. Even though more research needs to be done on the subject, results this far have been promising. Some questions regarding the topic were left unanswered, as the scope for the thesis had to be kept reasonable. How would the materials be affected by physical or chemical foaming, and how would these methods compare to expandable microspheres? How are different sections of a complex geometry parts such as gaskets foamed? Would a foamed gasket work in its real use?

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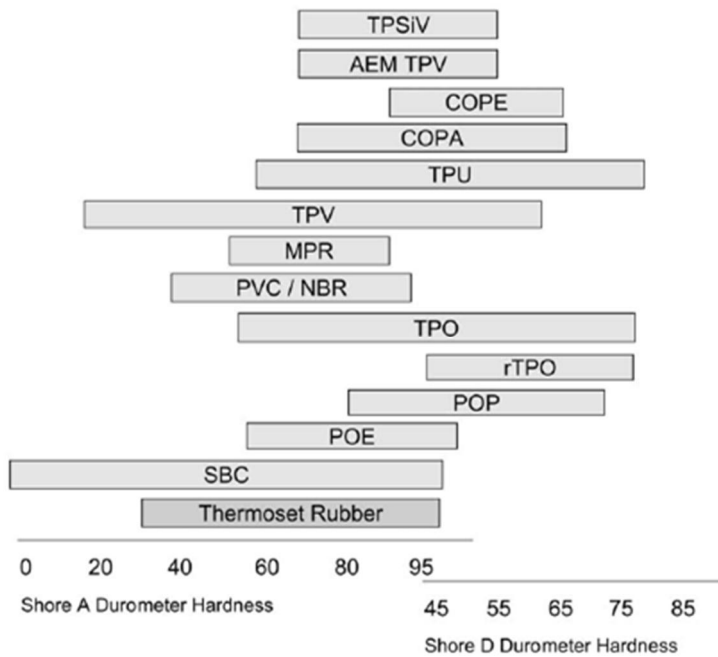
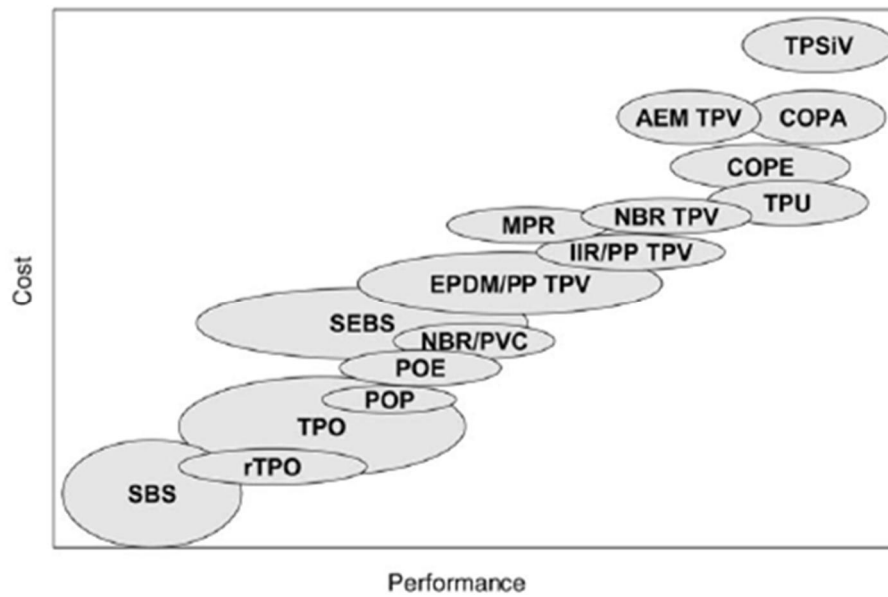
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APPENDIX 1. COMPARISON BETWEEN PROPERTIES OF TPES



[6]

APPENDIX 2. PROPERTIES OF BLOWING AGENTS

	Carbon Dioxide	Nitrogen	Oxygen
Chemical formula	CO ₂	N ₂	O ₂
CAS number	124-38-9	7727-37-9	7782-44-7
Molecular weight	44	28	32
Boiling point, °C	-78.3	-195.8	-183.0
Critical temperature, °C	31	-146.9	-118.3
Critical pressure, MPa	7.38	3.4	5.0
Liquid specific gravity at 25 °C	N/A	N/A	N/A
Heat of vapourisation at BP, kJ/mole	6.8	-	-
Gas conductivity mW/m ² K at 10 °C at 25 °C	15.3 16.4	24.6 25.8	25.2 26.6
Vapour pressure, kPa at 10 °C at 25 °C	4502 6434	Very high	Very high
Flammable limit in air (vol.%)	None	None	None
TLV or OEL, ppm	N/A	N/A	N/A
ODP (CFC-11 = 1)	0	0	0
GWP (with CO ₂ = 1)	1	N/A	N/A
Atmospheric lifetime, years	120	N/A	N/A

Description	Type	Decomposition temperature, °C	Gas yield @STP x 10 ⁻³ m ³ /kg	Gases
Azodicarbonamide (ADC)	Exo	200-230	220-245	N ₂ , CO, NH ₃ , O ₂
4,4-Oxybis(benzenesulfonylhydrazide) (OBSH)	Exo	150-160	120-125	N ₂ , H ₂ O
<i>p</i> -Toluenesulfonylhydrazide (TSH)	Exo	110-120	110-115	N ₂ , H ₂ O
<i>p</i> -Toluenesulfonylsemicarbazide (TSS)	Exo	215-235	120-140	N ₂ , CO ₂
Dinitrosopentamethylenetetramine	Exo	195	190-200	N ₂ , NH ₃ , HCHO
Polyphenylene sulfoxide (PPSO)	Exo	300-340	80-100	SO ₂ , CO, CO ₂
Sodium bicarbonate	Endo	120-150	130-170	CO ₂ , H ₂ O
Zinc carbonate	Endo			CO ₂
Citric acid derivatives	Endo	200-220	110-150	CO ₂ , H ₂ O
5-Phenyltetrazole	Endo	240-250	190-210	N ₂

APPENDIX 3. TABLES OF TPV MICROFOAMING

Table 1. Microcellular TPV Tubular Profile Properties

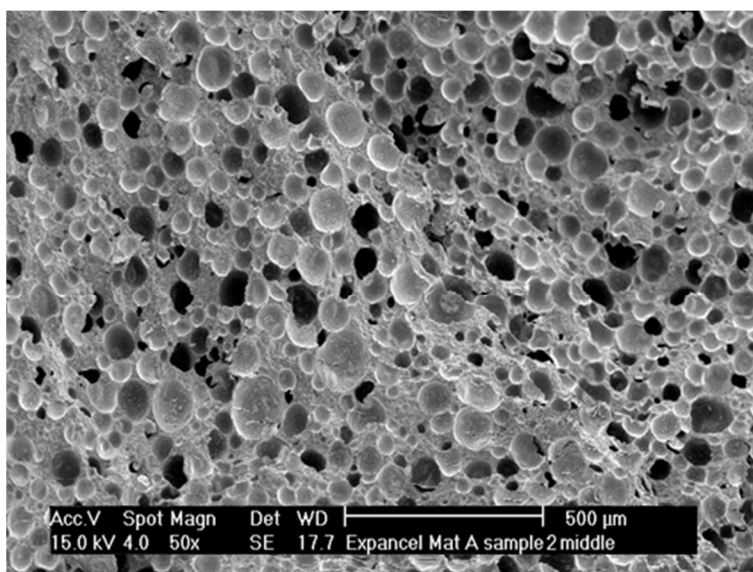
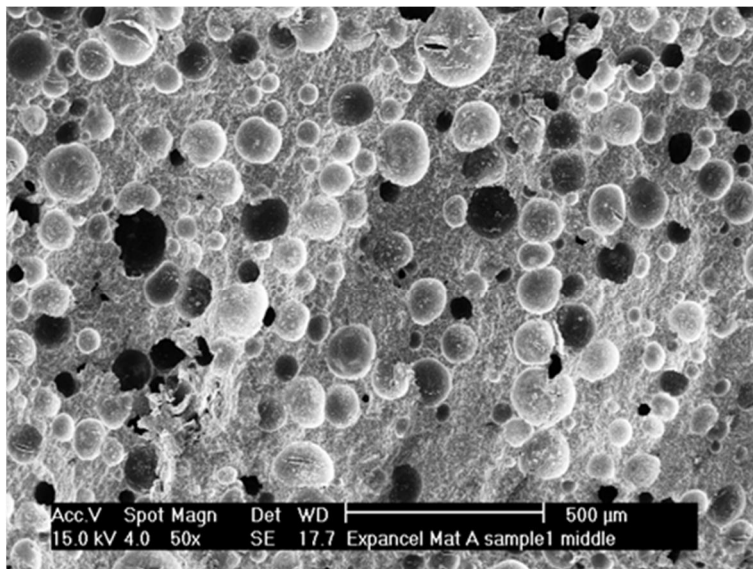
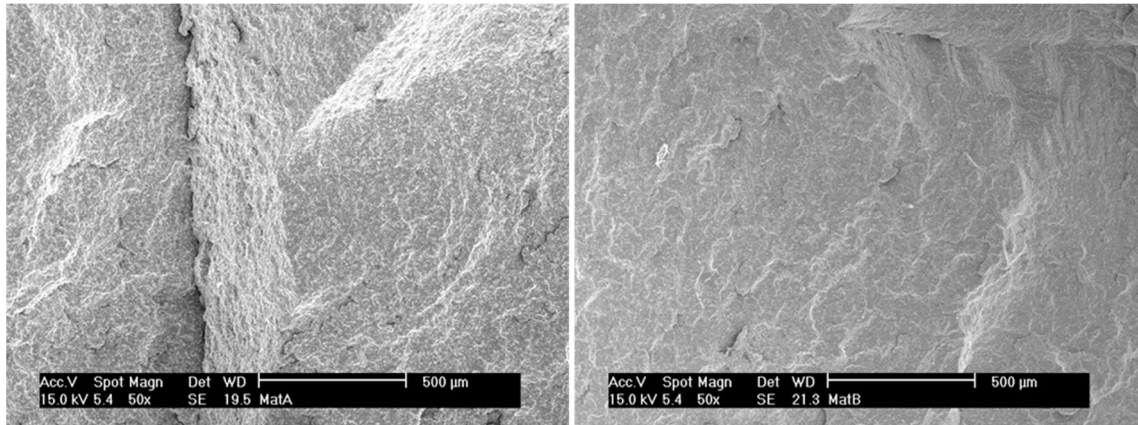
Property	Units	Sample				
		A	B	C	D	E
Durometer	Shore A	73	68	45	45	64
Solid Density	g/cc	0.95	0.95	0.90	0.91	0.99
Foam Density	g/cc	0.58	0.60	0.59	0.56	0.57
Wall Thickness	mm	2.0	2.0	1.7	1.8	1.9
C-set, 50%	%	40	41	38	37	43
Water Absorption	%	2.3	0.2	0.1	1.6	3.2
Cell Size	μ	50	70	50	80	200

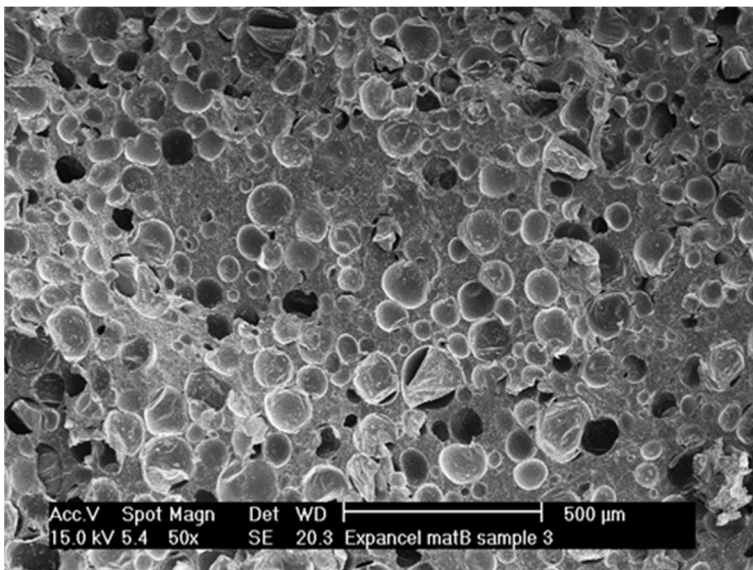
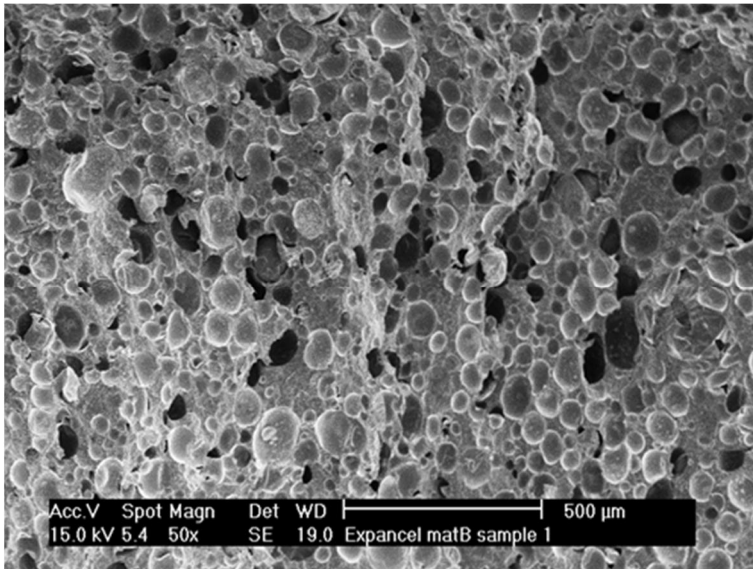
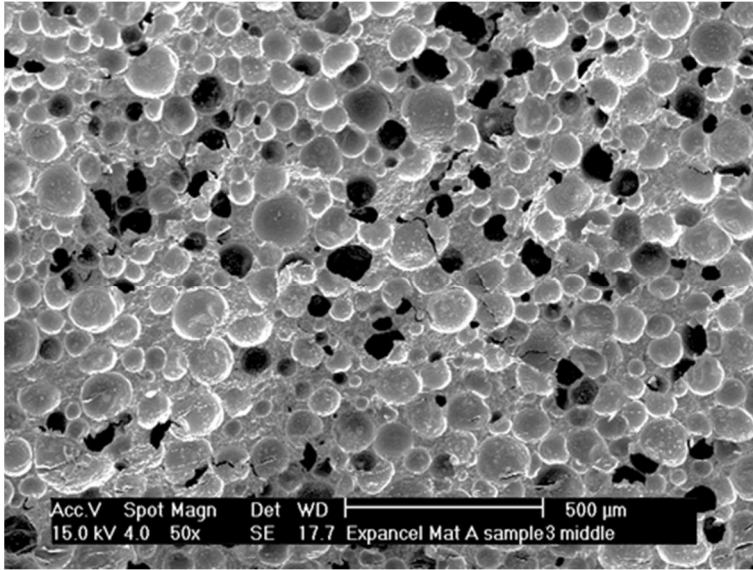
Table 2. Typical Performance of TPV Omega Profiles Foamed with Different Processes

Criteria	OEM Req't	EPDM Sponge	Microcellular TPV Foam	Other TPV Foam (CBA or H ₂ O)
Water Absorption	√	< 5%	0.1 – 5%	50+%
Compression set	√	< 30 – 50	< 40%	< 32 – 57
CLD	√	< 20 N/100 mm	< 20 N/100 mm	14 – 22 N/100 mm
Density range	√	0.40 – 0.70	0.40 – 0.70	0.50 – 0.70
Appearance	√	Smooth	Smooth	Smooth
Cell Structure		Heterogeneous	Homogeneous	Heterogeneous
Avg. Cell Size		150 – 250 μ	50 – 70 μ	> 100 μ

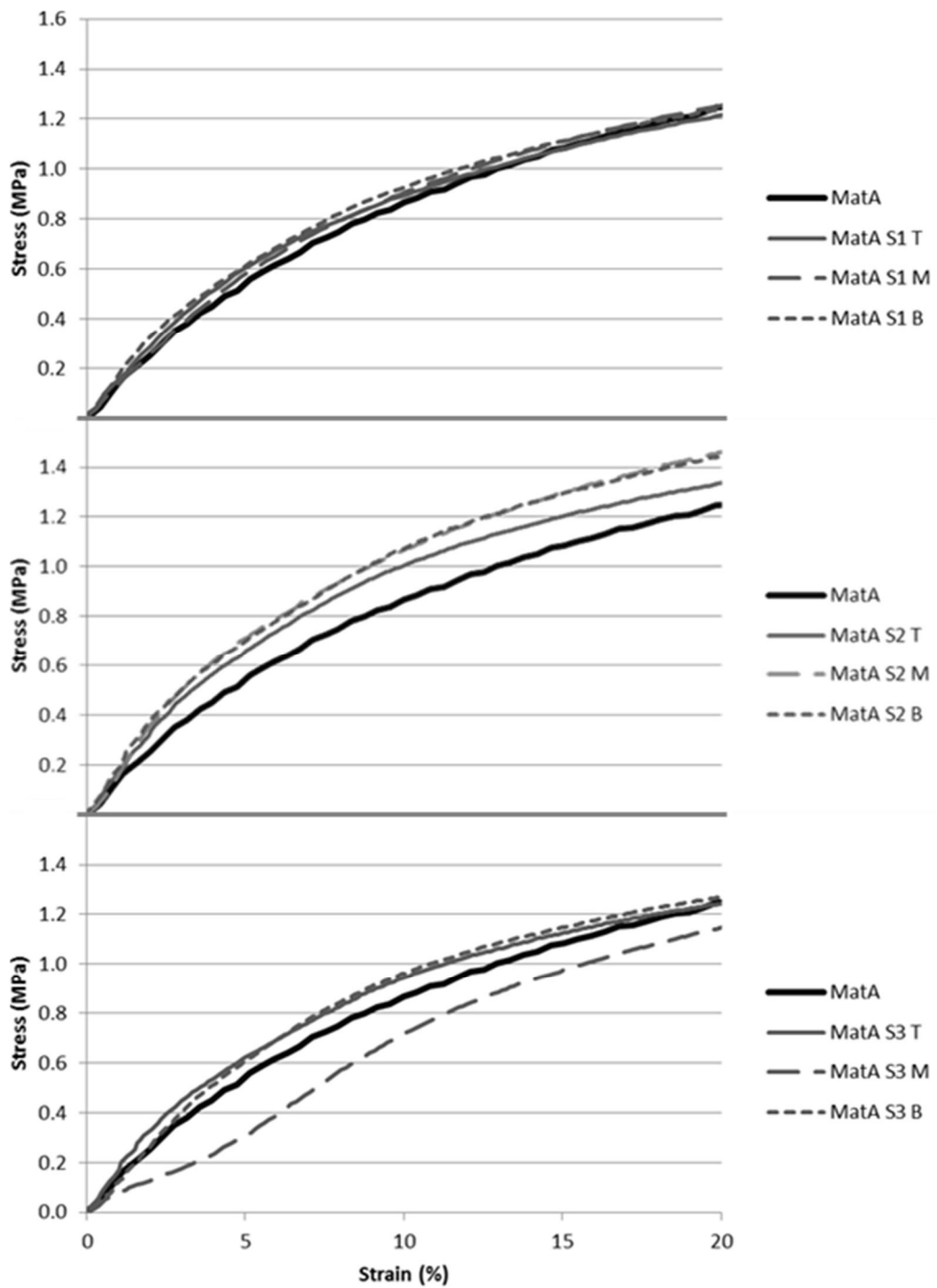
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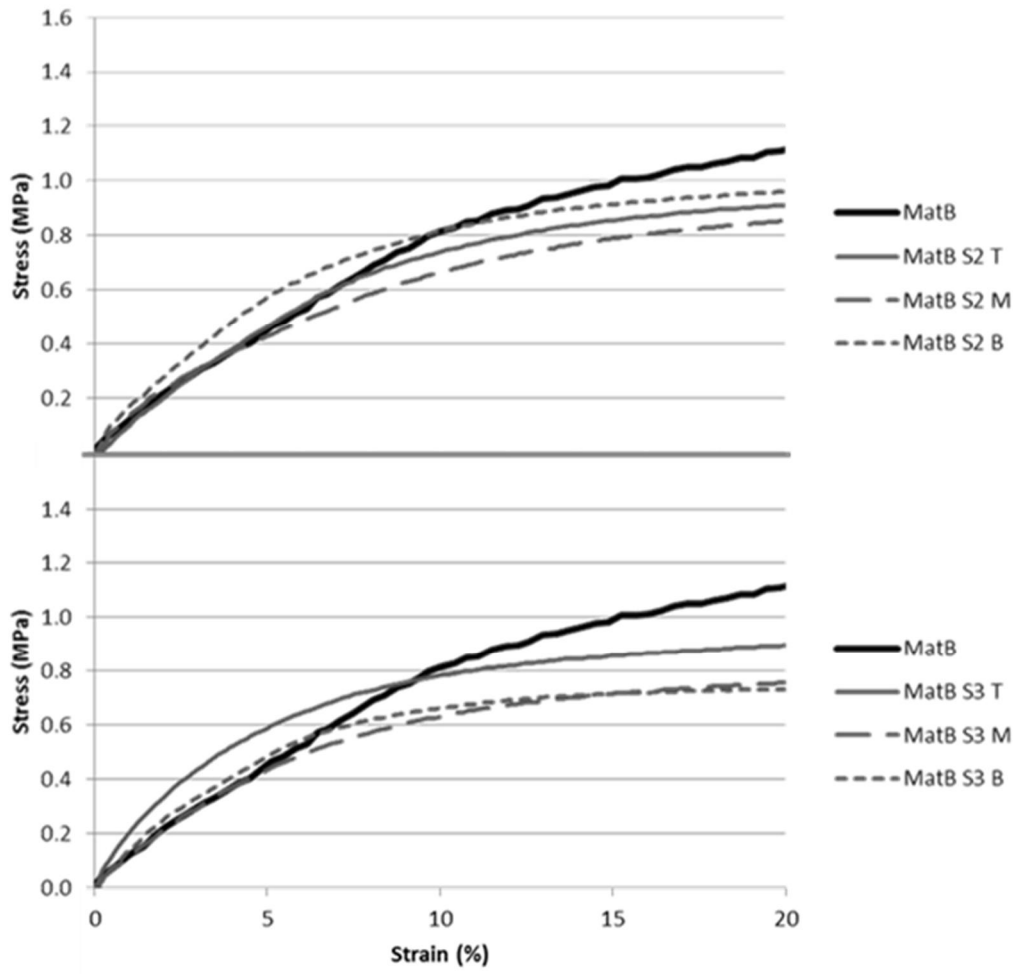
APPENDIX 4. SEM-PICTURES OF FOAMS AND SOLID MATERIALS





APPENDIX 5. STRESS-STRAIN CURVES





APPENDIX 6. TABLE OF FLAMMABILITY RESULTS

	Thickness (mm)	Sample	t1(s)	t2(s)	t3(s)	C1	C2	C3	C4	C5
MatA	3	1	0	0	0	0	0	0	No	No
		2	0	0	0	0		0	No	No
		3	0	0	0	0		0	No	No
MatA S1	5	1	0	0	2	0	0	2	No	No
		2	0	0	0	0		0	No	No
		3	0	0	2	0		2	No	No
MatA S2	5	1	0	0	0	0	0	0	No	No
		2	0	0	0	0		0	No	No
		3	0	0	0	0		0	No	No
MatA S3	5	1	0	0	2	0	0	2	No	No
		2	0	0	0	0		0	No	No
		3	0	0	0	0		0	No	No
Mat B	3	1	0	0	1	0	2	1	No	No
		2	0	1	5	1		6	No	No
		3	0	0	0	0		0	No	No
MatB S2	5	1	0	5	0	5	15	5	No	No
		2	0	2	0	2		2	No	No
		3	0	2	0	2		2	No	No
MatB S3	5	1	0	4	0	4	13	4	No	No
		2	0	2	0	2		2	No	No
		3	0	2	0	2		2	No	No

C_x = Criteria for classification [53]

C1: Afterflame for each individual specimen (t1 or t2). Maximum value of all tested specimen.

C2: Total afterflame time for any set ($\sum t1+t2$). Total sum, calculated to match a set of five specimens.

C3: Afterflame and glow after 2nd burn for individual specimen (t2+t3). Max. value of all specimens.

C4: Afterflame or glow for any specimen up to the holding clam. Most radical behaviour.

C5: Cotton indicator ignited by flaming particles or drops. Most radical behaviour.