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# FUNKČNÍ POLYMERNÍ PĚNY
FUNCTIONAL POLYMER FOAMS

DIPLOMOVÁ PRÁCE
MASTER'S THESIS


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BRNO 2018

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
FAKULTA CHEMICKÁ

# Zadání diplomové práce

| | |
|---|---|
| Číslo práce: | FCH-DIP1173/2017 |
| Ústav: | Ústav chemie materiálů |
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| Akademický rok: | 2017/18 |

## Název diplomové práce:

Funkční polymerní pěny

## Zadání diplomové práce:

Nalezení technologického postupu a složení vstupního materiálu umožňujícího připravit polymerní pěny s gradientem porozity a složení pro získání specifických funkcí.

## Termín odevzdání diplomové práce: 7.5.2018

Diplomová práce se odevzdává v děkanem stanoveném počtu exemplářů na sekretariát ústavu. Toto zadání je součástí diplomové práce.

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V Brně dne 31.1.2018

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## Abstract

Functional polymer foams are considered as a promising field which could potentially produce foams with added value. Specifically, functionally graded foams are materials which are expected to provide better mechanical properties while preserving low density in comparison with regular foams. In this thesis, a preparation process of such foams is designed, examination of prepared structure and comparison of mechanical properties with regular foams is performed. The obtained results are discussed and further research in this field is proposed.

## Abstrakt

Funkční polymerní pěny jsou slibnou oblastí výzkumu, která by mohla potencionálně produkovat pěny s vyšší přidanou hodnotou. Konkrétním příkladem jsou pěny s funkčním gradientem porozity. Očekává se, že tyto pěny dosáhnou lepších mechanických vlastností při zachování nízké hustoty, než je tomu u běžných pěn. Tato práce se zabývá navržením postupu přípravy těchto pěn, zkoumáním struktury a srovnáním mechanických vlastností s běžnými pěnami. Získané výsledky jsou diskutovány a jsou navrženy možnosti dalšího výzkumu v tomto odvětví.

## Key words

Cellular solids, blowing agent, polystyrene, citric acid, functional materials, functionally graded foam, pore-size gradient.

## Klíčová slova

Porézní pevné látky, nadouvadlo, polystyren, kyselina citronová, funkční materiály, funkční gradientní pěny, gradient porozity.

## Citation

HÁNA, T. *Funkční polymerní pěny.* Brno: Vysoké učení technické v Brně, Fakulta chemická, 2018. 50 s. Vedoucí diplomové práce prof. RNDr. Josef Jančáři, CSc.

## Declaration

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## Acknowledgment

I would like to thank my supervisor prof. RNDr. Josef Jančář, Csc. for his supervising and advices throughout my work on this diploma thesis. Also, I would like to thank my friends for their help and support.

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# 1. INTRODUCTION

There is a great interest in a development of porous materials nowadays. The reason is its versatility, which arise from their cellular structure and gives them a wide range of functional properties for numerous fields of applications. Foams are an effective material for thermal insulation, sound absorption, filtration, controlled drug release, tissue engineering scaffolds, as well as structural materials used in sporting goods and construction components in vehicles or protective media used for impact energy absorption. [1–4]

Another reason of wide variety use of foams is their low weight which goes hand in hand with use of foams made from polymer matrices. Polymers, in last decades, take place of construction materials with higher densities, such as metals. Foaming of polymers provides another way of decreasing a weight of construction materials, which is desired in current transportation industry. Low weight of components lowers fuel consumption, which improves emission rates of vehicles. Government regulations requires lowering emission rates from year to year and automotive companies must adjust their production to these regulations, so application of foamed materials is a must. Also, expansion of electric cars requires low weight materials, which allows them drive longer distances without need of recharging their batteries. [1–4]

Protective elements in fields of automotive industry and personal protection requires high-energy absorption materials in combination with low density, such as cellular materials. Such materials possess the capability of undergoing a prolonged stress plateau over a large percentage of a total strain. [1–4]

Relatively new materials are functionally graded foams. These foams have non-homogenous composition and controlled, graded micro structure. They can be applied in fields of aerospace, bio medicine or automotive industry. Research is focused on a preparation of such materials and improving a control of a structure with effort of improvement of properties. Functionally graded foams provide better mechanical, thermal or sound absorption properties with same or lower density as regular foams. Combination of improvement of their properties and lowering of density makes them interesting material for researchers on one side and companies from mentioned fields on other side and it is also the reason of this thesis. [1–4]

# 2. THEORETICAL PART

## 2.1. Polymer foam types and description

Polymer foams or cellular polymers are expanded thermoplastic or thermoset materials made from two or more phases. One phase is a polymer matrix, and the second phase is a gas in form of cells. Different types of other particles can be added, such as nucleating agents, which role is an initiation of a cell growth, or some types of fillers for obtaining special properties. For example, carbon nanofillers with purpose of increasing an electric conductivity of a foam. [5–8]

Polymeric foams are classified into two categories, which depend on type of cells. Open-cell and closed-cell foams are recognized. Open-cell foams are usually flexible materials, where cell walls are broken, and the structure consists mainly of ribs and struts (Figure 1). Closed-cell foams are generally more rigid than open-cell foams. Cells are isolated, and cavities are surrounded by complete cell walls (Figure 2). If a foam is flexible or rigid depends also on type of material, which is used for their production. Two main types of material for polymeric foams are thermoset and thermoplastic matrices, these categories are described in following chapters. [5, 6, 8, 9]

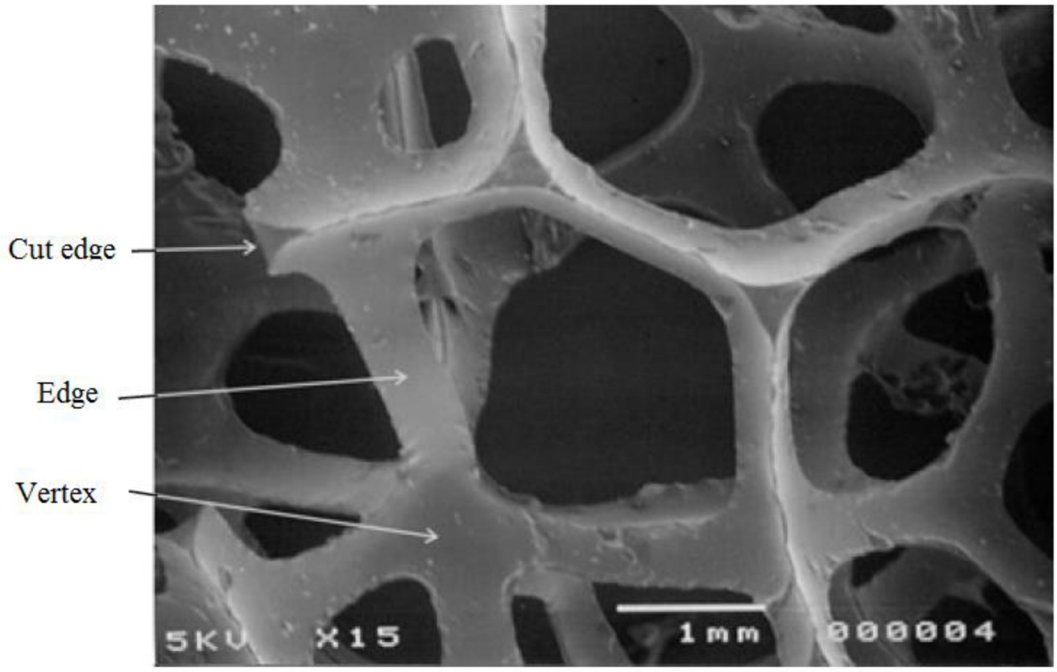


*Figure 1: Photograph of polyurethane (PU) open-cell foam with density 28 kg m$^{-3}$; scanning electron microscope (SEM). [9]*

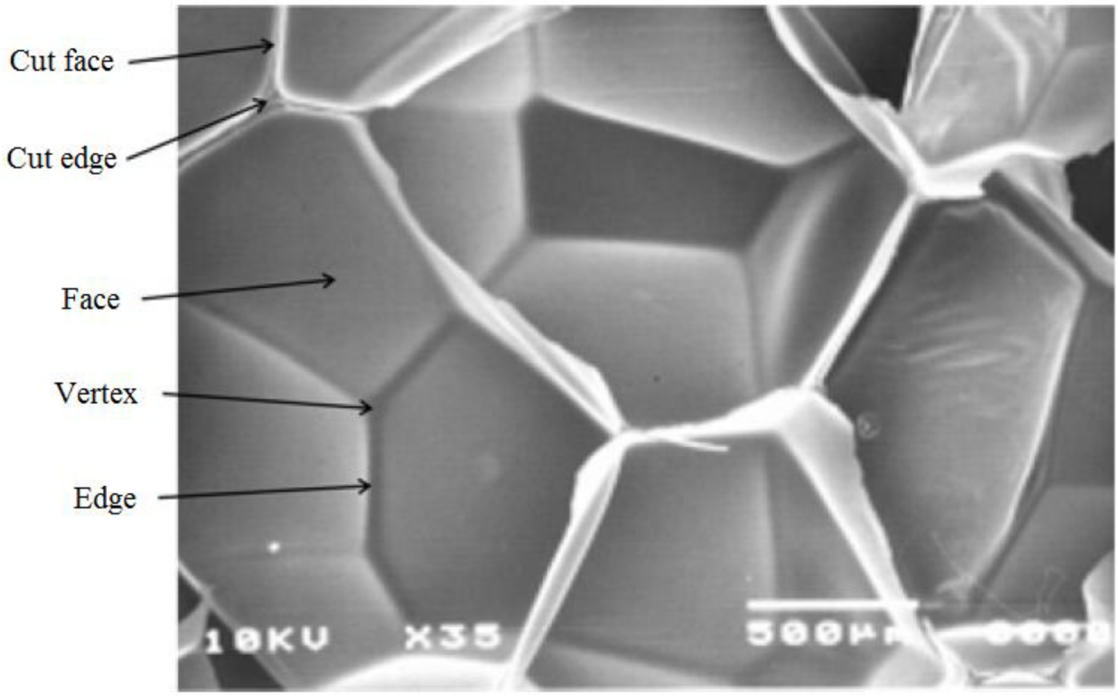


*Figure 2: Photograph of low density polyethylene (LDPE) closed-cell foam with density 24 kg · m$^{-3}$; SEM. [9]*

Another classification is based on a cell size. In this context, foams are categorized in four main groups, conventional, fine-celled, microcellular and nanocellular. Specification of these groups is listed below in Table 1. [5, 6, 10]

Table 1: Foams classification. [10]

| Foam type | Cell size (μm) | Cell density (cells · cm$^{-3}$) |
|---|---|---|
| Conventional | > 300 | < $10^6$ |
| Fine-celled | 10-300 | $10^6$–$10^9$ |
| Microcellular | 0.1–10 | $10^9$–$10^{15}$ |
| Nanocellular | < 0.1 | > $10^{15}$ |

Different cell size provides different properties of a foam, mechanical, optical also thermal properties depend on a cell size. Current research is focusing on micro and nanocellular foams. Nanocellular foams are possible to use as thin films thanks to size of cells, also nanofoams are expected to have superior properties to those of existing materials, such as a higher strength-to-weight ratio. Unfortunately, synthesis of nanocellular foams is a difficult task, one way is dispersing nanoparticles into polymer, these act as a nucleating agent for formation of cells in units of nanometers. [6, 8, 11]

### 2.1.1. Thermoset foams

Thermoset foams are crosslinked and therefore their properties differ from thermoplastic foams, also a processing of these foams is different.

- **Polyurethane foams**

The most common thermoset foams are made of PU. PU is produced by reaction of di-isocyanate and diol (Figure 3) or polyol. Reaction of multifunctional alcohols will produce crosslinked structure:

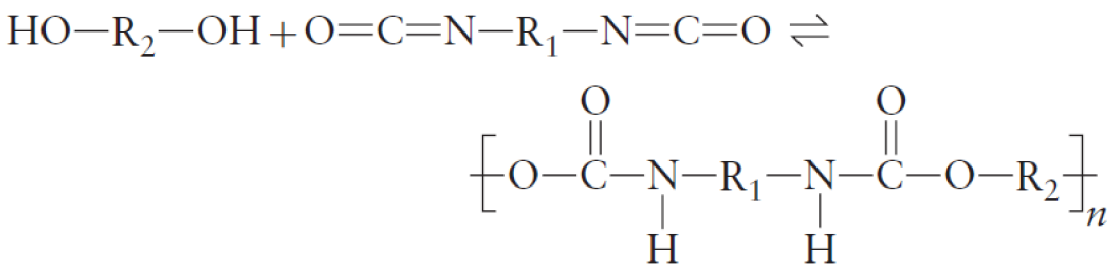

*Figure 3: Reaction scheme of PU formation. [9]*

However, a polymer produced this way isn´t foamed. It is necessary to add 1–4 % of water content to create porous structure. Water reacts with di-isocyanate monomer to produce $CO_2$ (Figure 4), which acts as a blowing agent:

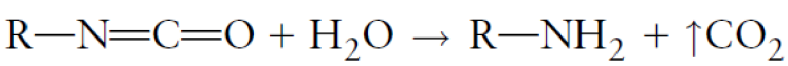

*Figure 4: Reaction scheme of $CO_2$ formation. [9]*

Addition of more than 5 % of water may cause overheating and degradation of a foam, so in, order to form low-density foam, a physical blowing agent must be used. Either, flexible or rigid foams are prepared depending on a cell structure (open/closed cells). PU foams are used for cushioning, thermal and sound insulation, in construction applications etc. [9, 12]

- **Syntactic foams**

Another type of thermoset foams are syntactic foams. Syntactic foams are basically composite materials, which consist of a matrix and a filler in form of hollow spheres. Thermoset polymer matrix used are epoxy or phenolic resins, polyimides and polyurethane. Fillers used are glass, carbon, metal, ceramic or resin microbubbles. These materials are classified as foams since their microstructure is similar, to a cellular, gas-expanded, solidified liquid. Syntactic foams are classified as two- or three-phased materials, depends if matrix contains also dispersed air bubbles or not. [13–15]

Syntactic foams have low degree of water absorption, thermal properties depend mostly on polymer matrix used. Plastic deformation in compression and good hydrostatic pressure resistance are reasons for their use in a naval and a marine engineering. Syntactic foams are used, also, in deep sea applications, such as platforms, pipe joints or shielding of apparatuses.

Thanks to low weight, also, in aerospace engineering as fillers in alveolate structures or shielding for space vehicles and rockets. [13–15]

### 2.1.2. Thermoplastic foams

Thermoplastic polymers are divided into two groups, amorphous and semi-crystalline, depending on their chemical structure and processing conditions.

- **Semi-crystalline foams**

Semi-crystalline structure is observed in polymers with linear and regular structures which allows them to fold their polymer chains to form crystalline formations, such as spherulites which are common for polypropylene (PP). Semi-crystalline polymers are described as two-phase systems consisting of crystallites dispersed in an amorphous matrix. A number of crystallites depends not only on structure of a certain polymer, but also on thermal and processing history of a material. If polymer was cooled with high speed in a short period of time, polymer chains couldn´t have enough time to form a crystallites and structure would me more amorphous, than if cooled slowly. Typical semi-crystalline polymers are PP, high-density polyethylene (HDPE) and polyethylene terephthalate (PET). The absorption and diffusion in semi-crystalline polymers takes place almost exclusively throughout amorphous regions. Therefore, produced foamed structure isn´t uniform and is affected by a morphology of a polymer. In the Figure 5 can be seen an irregular cell structure formed due to crystalline areas of PP. To minimize this effect and obtain the most uniform structure possible semi-crystalline polymers must be foamed above the melting point of crystalline regions. Unfortunately, degradation quickly takes place above this temperature and it is necessary not to keep polymer above its melting temperature for a long period of time. [9, 16, 17]

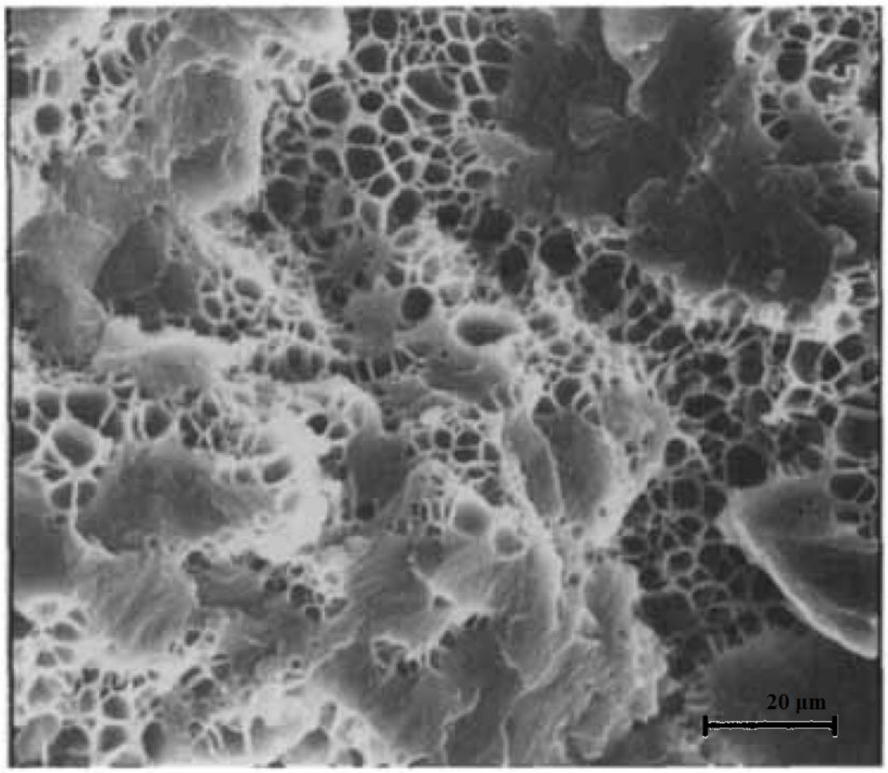


*Figure 5: Photograph of foamed PP sample; SEM. [16]*

- **Amorphous foams**

Amorphous polymers, on the other hand, have an irregular structure or branching of the molecular chains which causes forming of an amorphous structure. The fluctuation of properties is minimal, because of uneven packing of chains. Typically used amorphous polymers are polystyrene (PS) or polymethylmethacrylate (PMMA). In cellular processing of amorphous polymers, nucleation of cells takes place homogeneously throughout the whole structure and the polymer expands uniformly, forming regular foamed structures. [9, 16, 17]

Earlier, a research was focused on foaming of amorphous polymers, but current research is focusing more on foaming of a semi-crystalline polymers, because of their mechanical properties and wide variety of use, especially, in automotive and generally in transportation industry. [9, 16, 18]

## 2.2. Foaming process

Individual stages in the development of cells (shown in the Figure 6):

1. Growth of spherical bubbles in a polymer melt, bubbles are isolated and have minimum surface area for a given volume.
2. Increasing volume of bubbles causes touching of bubbles and distortion of shape. Formation of a closed-cell foam.
3. When the faces in a closed-cell foam collapse, an open-cell foam is formed.
4. In low viscosity polymers may occur fusing of cells or even collapsing of cells back into liquid.

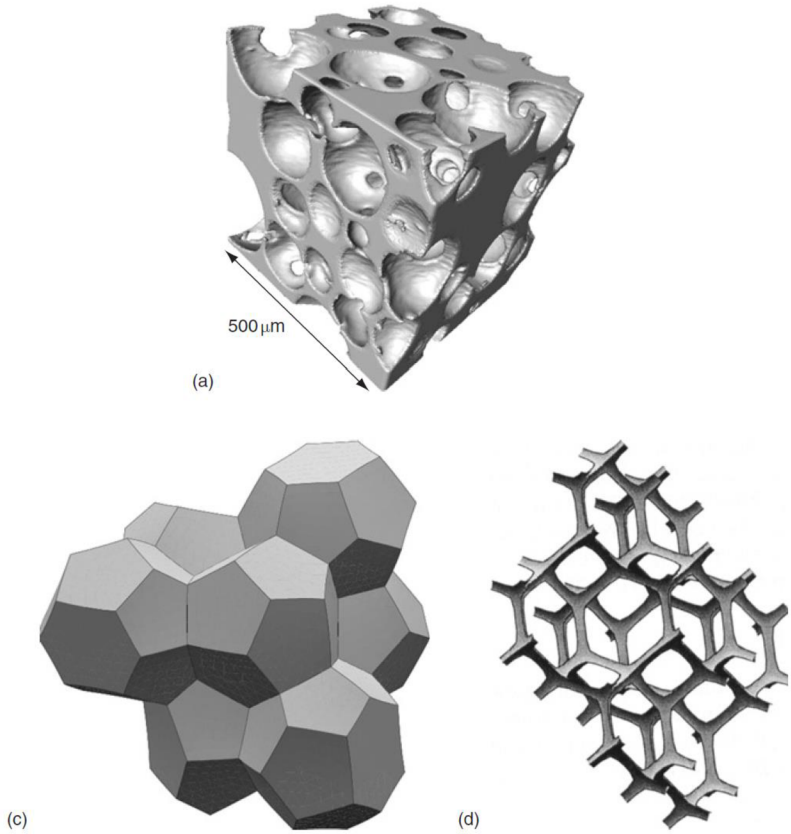


*Figure 6: Scheme of stages in the cell development a) isolated spherical bubbles, b) a closed-cell foam and c) an open-cell foam. [9]*

### 2.2.1. Bubble initiation

The development of bubble in a polymer melt is called nucleation. There are several possible sources of a gas for cell formation:

- Dissolved gas, which is normally present, or artificially added into a polymer melt. Or a solution forced into supersaturation by decreased pressure.
- Gas formed from a liquid with low boiling temperature, which is incorporated into a matrix as a blowing agent, released by increase of a temperature or a pressure decrease.
- Gas produced by a chemical reaction, such as in PU foaming.
- Product of a decomposition of a chemical blowing agent.

Bubble nucleation is affected by temperature, pressure, humidity of matrix and environment, parameters of filler particles, presence of nucleating agents, rate of gas generation and impurities. All these aspects must be taken into a consideration while producing foamed structure. [8, 9]

### 2.2.2. Bubble growth

The initial bubble is a sphere, in ideal conditions, that grows because of a different internal and external pressure ($\Delta p$). Interfacial surface tension ($\gamma$) also affects bubble growth. The radius ($r$) of a bubble at equilibrium is described as (1):

$$\Delta p = \frac{2\gamma}{r} \tag{1}$$

The rate of growth of a cell also depends on viscoelastic properties of a matrix, the blowing agent pressure, the cell size and the permeation rate of blowing agent through the matrix. Bubbles are enlarged by a diffusion of gases coming out of a solution into existing bubbles, coalescence of smaller bubbles, and thermal effects on internal bubble pressure. With increasing volume of bubbles their shape is distorted into polyhedral. [8, 9]

### 2.2.3. Bubble stabilization

Wall-thinning effect takes place as the cell walls are squeezed into polyhedral. Liquid is drained into lines and starts form ribs and struts. Cell wall thinning can continue to the point where cell walls collapse and form open-cell structure. Ultimate stabilization is effect of the physical cooling below second-order transition point, this prevents polymer flow and freezes the structure of a foam. Other possibility, of structure stabilization, is a chemical reaction resulting into forming crosslinking. Previously formed bubbles solidify in a certain phase of bubble growth. [8, 9]

## 2.3. Porous structure preparation

Over the last few decades, there have been developed several preparation methods of obtaining porous structure in a polymer matrix. Various methods can be used depending on polymer type, size and shape of desired cells and the final application. Below are described main techniques of preparation methods. [6, 10]

### 2.3.1. Blowing agents

The gaseous phase in foams can be formed either by decomposition or reaction of certain substance (chemical blowing agents, CBAs) or by release of dissolved gas in a polymer melt (physical blowing agents, PBAs). [6, 10]

- **Chemical blowing agents**

CBAs either take part in chemical reaction forming gaseous product, which than form cells (for example reaction of water with isocyanate in PU foaming, see chapter Thermoset foams) or decompose at certain temperature to form a gas. The second type of CBAs are substances such as azo-hydrazine and other nitrogen-based materials (used in thermoplastic and elastomeric foams), sodium bicarbonate (for thermoplastic foams) also organic acids are used (such as citric acid). The decomposition reaction of sodium bicarbonate (2) according to [19]:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \tag{2}$$

Decomposition of citric acid consists of two reactions (3) and (4) according to [19]:

$$C_6H_8O_7 \rightarrow C_6H_6O_6 + H_2O \tag{3}$$
$$C_6H_8O_7 \rightarrow C_5H_6O_4 + CO_2 \tag{4}$$

CBAs are used for forming both closed and open cell foams. Gaseous products formed are, depending on a substance used, nitrogen, carbon dioxide, carbon monoxide, ammonia and others. Foaming using CBAs is an irreversible process. In past, there was a large use of chloroflourocarbons as CBAs, but these were banned, because of ability of their products to decompose ozone, which causes some of current environmental issues. [6, 10]

- **Physical blowing agents**

PBAs are inert gases which don´t react with a polymer matrix. Mainly used are nitrogen and carbon dioxide, but also organic gases such as propane, butane or pentane. Procedure to produce foamed polymer is first saturate the polymer with certain gas at elevated pressure, then heating the material to its glass transition temperature, reducing the pressure to a state where polymer is supersaturated with inert gas, rapid nucleation of cells takes place and finally dropping temperature to prevent cell growth and escaping of gas out of the polymer. [6, 20]

Nowadays lot of PBAs are used in form of supercritical fluids, mainly in case of carbon dioxide. Dissolution of supercritical carbon dioxide in polymer melt leads to decrease of viscosity, melting point and glass transition temperature, which simplifies processing of polymer. [6, 20]

Foam production may be either continuous or discontinuous process. A continuous process is limited to polymers which are good melt-processed. These foams can be produced by melt extrusion or injection molding process in their molten state. Discontinuous techniques are related to no melt-processable and thermally decomposed polymers. [6, 10, 20]

### 2.3.2. Other techniques

In following paragraphs there are described another process of preparation of porous structures.

*Phase separation* is a method for which it is necessary to have binary or multicomponent polymer, suitable solvent and additive mixtures if needed. One of the polymer components is dissolved in a solvent, which is subsequently removed from a matrix leaving a foamed structure. This technique is limited to non-crosslinked polymers. Depending on a process conditions either open or closed cell foams can be prepared with cell size ranging from 0.1 nm to 100 µm. [6]

The *leaching* method consists of selective leaching of inorganic salts such as NaCl or KCl or of an organic compound, for example glucose or gelatin microspheres. These are used as porogens which generate pores. Polymer is first dissolved in a highly volatile solvent, then casted into a mold containing a solid porogen. Solvent is evaporated and the porogen is washed out leaving a foamed structure. Figure 7 shows a simple schema of a preparation of graded foam with a particulate leaching technique. [6, 21]

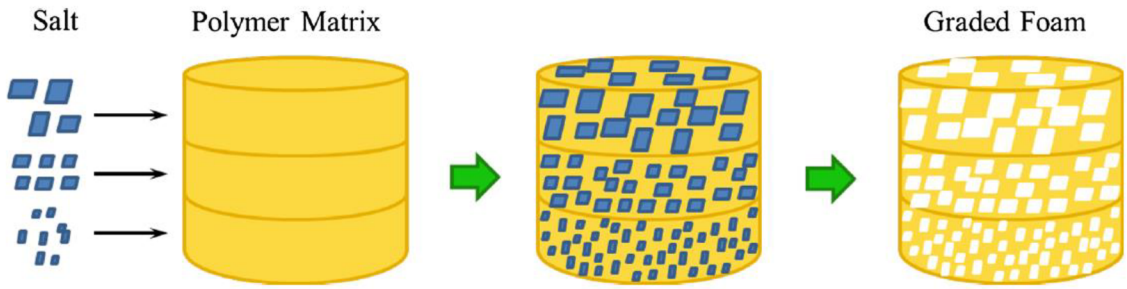


*Figure 7: Scheme of a preparation of graded foam using particulate leaching technique. [21]*

The problem with this method is contaminations of matrix with solvent or porogen residues. To overcome disadvantage of this method melt-molding/particulate leaching method is used. Polymer is melted, mixed with solid porogen and hot-pressed together. Porogen is washed out after cooling the matrix. The advantage of this method is control over pore size, structure and porosity by the size, shape and distribution of porogen particles. [6]

*Etching* is a method where a polymer is exposed to a high-energy radiation, which induces chain scission and leaves damaged polymer molecules. Polymer film is then etched by an acid or an alkaline solution which eliminates loose polymer parts. This technique can be even used for removing inorganic particles present in a polymer composite leaving porous structure. There are currently commercially available etched membranes made of polycarbonate or polyester. [6]

*Thermal decomposition* can be used either for a block copolymer consisting of thermally stable and thermally labile block or thermally stable polymer filled with thermally labile organic component. In both cases a sample is exposed to a high temperature in, order to decompose thermally labile part. This technique is limited to polymers with high temperature stability, such as a polyimide or a polyamide. [6, 22]

Less often techniques for preparing porous structures are for example *stretching* and *sintering*. Stretching is a method where a semi-crystalline polymer is stretched until an amorphous parts aren´t deteriorated and pores are produced. Sintering technique consists of mechanical compression of polymer particles at elevated temperature. [6]

## 2.4. Foam production technology

In following paragraphs, there are described the most used technologies for production of foamed materials. [8, 23]

- **Foam extrusion**

Continuous technique enabling production of large quantities of foamed thermoplastic polymer sheets, profiles, pipes etc. Physical or chemical blowing is used for forming of a foamed structure. CBAs are premixed with polymer pellets and fed to the extruder. CBA is decomposed in the extruder and evolving gas dissolute in polymer melt. PBAs (gas or liquid) are injected into polymer melt through the vent port approximately two-thirds of the way between the feed throat and die and PBA dissolute in polymer melt. It is necessary to prevent premature foaming inside the extruder. As the molten polymer leaves the die, the reduced melt pressure allows gas to expand and creates a porous structure. Temperature drop freezes created structure of the foam. [23–25]

- **Foam injection molding**

Foam injection molding is similar as standard injection molding, which allows production of foamed thermoplastic components on commercially available injection molding machines. Polymer pellets along with blowing agent is fed to the extruder in a similar way as explained in chapter above (Foam extrusion). A large pressure drop between the plasticization unit and tool cavity induces the melt to foam and formation of foam is achieved by gas evolution inside the polymer melt. In the picture below (Figure 8) is simple process description. [23, 26]

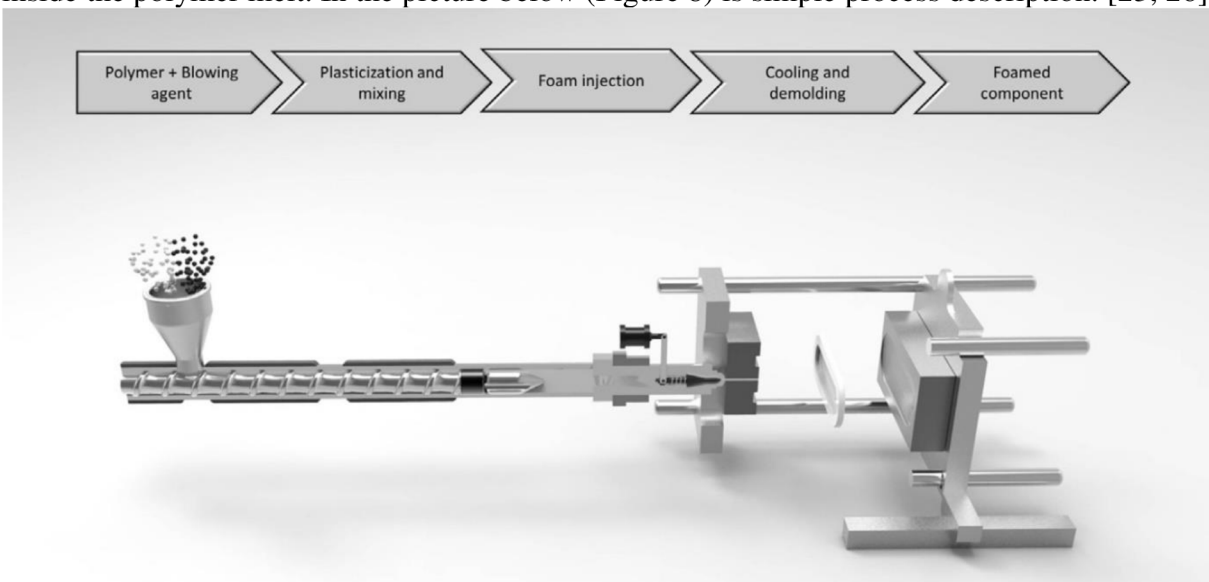


*Figure 8: Simple description of the process chain for foam injection molding [26]*

- **Pour foaming**

Using this technique doesn´t put much pressure on the material and mold, so it doesn´t need much strength. Low pressure allows production of large products, however, these products have low strength and bad dimensional precision, so this technique cannot be used for production of structural components. It is mainly used for thermoset polymers with good foamability such as PU, ureaformaldehyde, phenolic, polyvinyl, epoxy or organosilicone. Raw materials must be mixed completely and then poured into a mold with no or small pressure. [23]

- **Mold pressing**

The foam material is placed into a mold and then heated and pressed. The process includes two parts: mixing and molding. The mixing facility includes a kneader, a plastic mixer, an internal mixer, and an extruder. The molding facility can include a hydropress, a digester, and a mold. One-step and two-step approaches are distinguished. One-step process is to put the material with foaming agent into a mold and then proceed pressing, polymer is foamed and shaped in one step. Other way is to pre-foam a polymer then put pre-foamed polymer into a mold and press it to obtain desired shape. [23]

- **Reaction injection molding (RIM)**

In this process, highly reactive substances are mixed under high pressure and injected into a mold to react, polymerize and turn into foamed material. Workflow chart is shown in the picture below (Figure 9). It can be used for foaming of PU, ureaformaldehyde, nylon, styrene class resin and epoxy resin. [23]

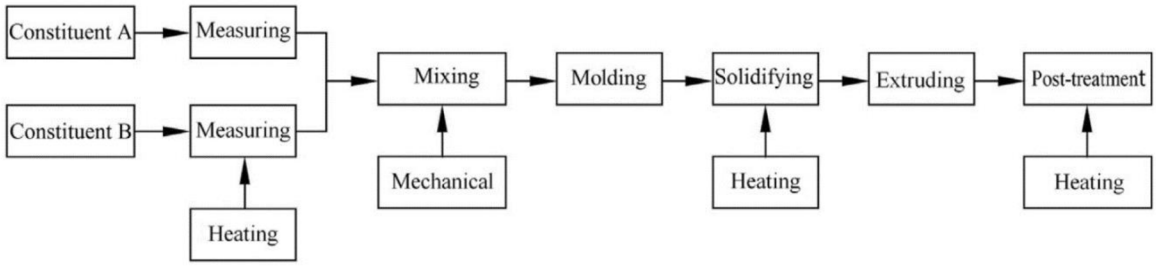


*Figure 9: Workflow chart for the RIM process. [23]*

- **Expansion method**

The expansion method is special method used for PS foaming. The method consists of preparation of PS beads, which contains blowing agent, nucleation agent and other additives depending on their target application. Surface treatment of the beads is possible. PS beads are than heated by saturated steam above the glass transition temperature of PS and foamed by blowing agent. Those pre-foamed beads are cooled and put into a mold of desired shape than they are heated again directly in a mold and form homogenous foamed structure. [8]

## 2.5. Current research on functional polymer foams

Below is a summary of current research on the field of functionally graded polymer foams.

### 2.5.1. A functionally graded syntactic foam

Nikhil Gupta at Polytechnic University of Brooklyn prepared functionally graded structure for high energy absorption under compression consisting of glass microballoons in a polymer matrix. Structure is based on creating a gradient of wall thickness of microballoons (Figure 10). [27]

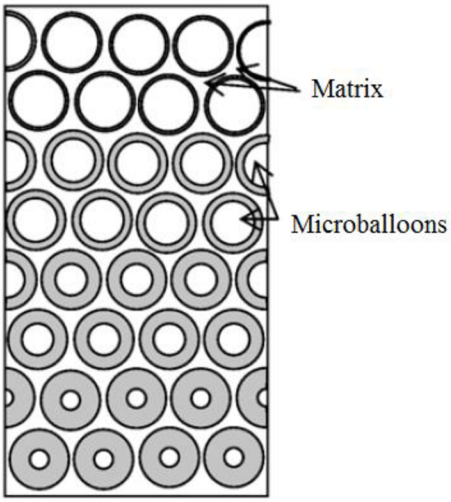


*Figure 10: Microstructure scheme of functionally graded foam. [27]*

Results show that the compressive modulus, strength and total energy absorption of such foams can be controlled by variation of type and volume fraction of microballoons. Prepared functionally graded syntactic foams are capable of withstanding 60–75 % compression without significant loose of strength or failure. The area under the stress-strain curves is 300–500 % larger compared to a plane syntactic foam. The compressive strength and modulus depend on a microballoon layer with thinnest walls. The authors suggest that it is desired to prepare such structure with smooth gradient instead of layered structure. [27]

### 2.5.2. Functionally graded PMMA foamed by supercritical $CO_2$

Changchun Zhou and his colleagues prepared functionally graded PMMA foams using supercritical $CO_2$ with a structure foam-solid-foam (Figure 11), also size of cells near solid region of samples is larger than size of cells at the surface of the sample. [28]

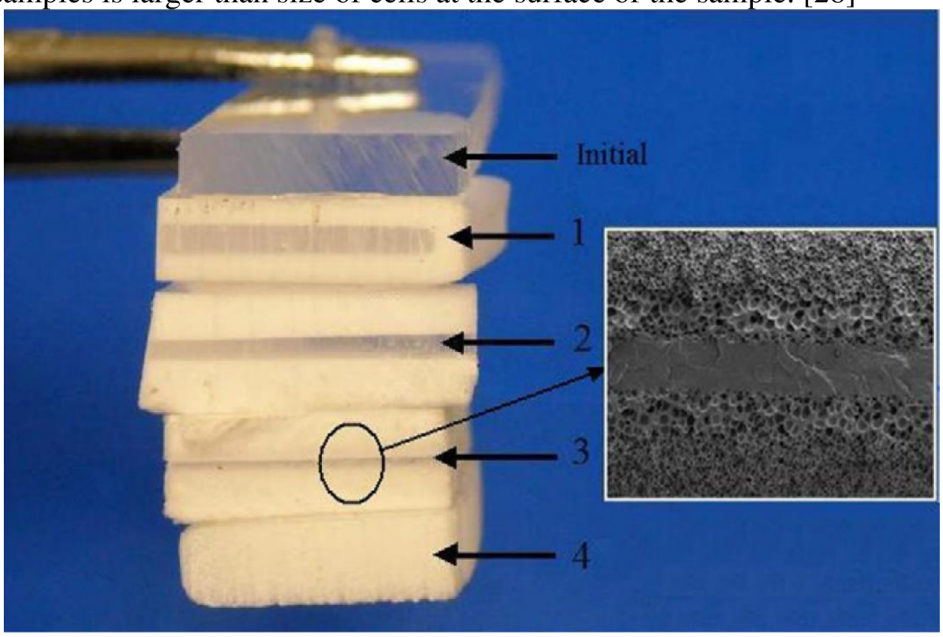


*Figure 11: Comparison of solid PMMA and foamed samples, the detail of interface of solid and foamed regions, SEM. [28]*

Mechanical properties of samples were measured by three-point bend test. According to results flexural modulus decreased with increasing foamed regions, but the flexural toughness of samples was the best for those with 65 % foamed regions. It indicates that a foam structure can be customized to meet certain requirements. [28]

### 2.5.3. Bio-based functionally graded foams for enhanced acoustic properties

Authors prepared functionally graded polylactide (PLA) foam by particulate leaching and compression molding technique using NaCl as a porogen. Aim of the study is an enhancement of sound isolation properties of the foam. An incorporation of a gradient of cell-size into the foam improves sound absorption capabilities by 20 % compared to uniform foam with the same porosity. Authors also compared mechanical properties such as compressive strength and modulus of prepared samples with standard foams (Figure 12). Results show slight increase of compressive modulus of functionally graded foams. [21]

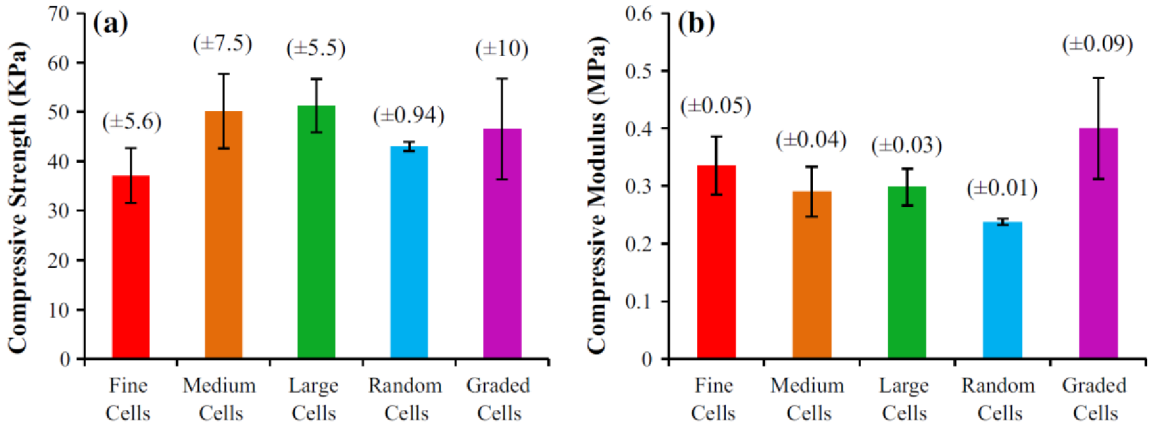


*Figure 12: Comparison of a) compressive strength and b) compressive modulus of graded foams and uniform foams. [21]*

### 2.5.4. Preparation of foams via thermally induced phase separation

The aim of this study is preparation of pore size gradient scaffold for tissue engineering, especially for bone tissue repair, using thermally induced phase separation (TIPS). A solution of poly-L-lacticacid, 1,4-dioxane and water in a plastic bag was placed into an experimental setup which provided different cooling rates on top and bottom side of the sample. Different cooling rates provided different times for nucleation and cell growth in a foam which formed a smooth cell size gradient inside the sample. Solvent was then rinsed with distilled water and sample was dried. Bellow (Figure 13) are shown obtained structures. [22]

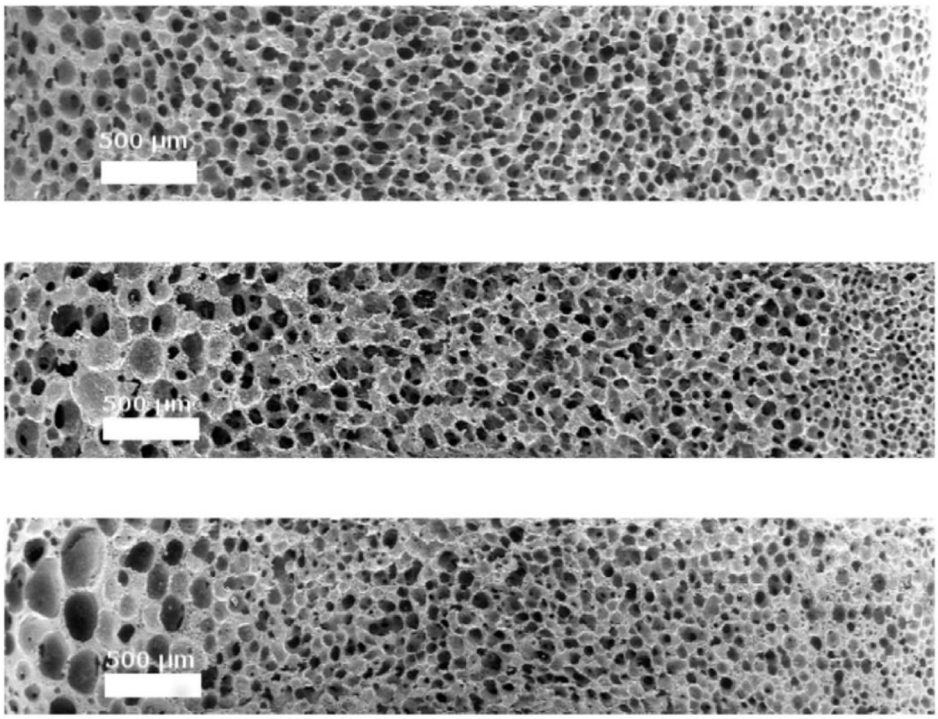


*Figure 13: SEM photographs of prepared samples at different demixing temperatures (in order 25, 30 and 35 °C), the left side was fast cooled and the right slow cooled. [22]*

## 2.6. Finite element analysis

Finite element analysis (FEA) is used to find the stress distribution in complex materials. There are two ways of FEA: static and dynamic. Static approach relates forces to deflections, but doesn´t consider the acceleration of mass. Dynamic analysis on the other hand, uses explicit method to estimate forces, apply them to the mass and calculate acceleration. Explicit FEA is elemental method to analyse impact problems. [9]

### 2.6.1. FEA material models

There have been done a lot of research in fields of FEA for metals and rubbers for their constitutive equations for deformation. Some of equations have been adapted for foams, without full validation. The two main types of foam material models:

- Non-linear elastic: the response is calculated from a strain energy function; these models are called hyperelastic.
- Elastic-plastic: compressive yielding causes permanent foam densification (crushing).

These FEA models are for isotropic materials and treats a material like a continuum. However, lot of foams are anisotropic and have complicated structure, which seems on a bigger scale homogenously. This means that modelling of real foams is approximate. [9]

### 2.6.2. Crushable foams

Permanent plastic deformation or a fracture occurs in crushable foams. This category includes PS, PP, PE and some rigid PU foams. Hardening mechanism, which is increase of yield stress with deformation, is due to the compression of the cell gas in closed cells. In contrast, metal hardening is a function of the cumulative strain history, understand the build-up of dislocation structures. [9]

- Yield surfaces

  Model for crushable foams is based on the von Mises yield criterion (5):

$$\sigma_e^2 \equiv \frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2] \tag{5}$$

  The von Mises equivalent stress $\sigma_e$ is a function of hydrostatic pressure according to (6):

$$\left[p - \frac{1}{2}(p_c - p_t)\right]^2 + \left(\frac{a\sigma_e}{b}\right)^2 = a^2 \tag{6}$$

  The yield surface in the $p$ vs $\sigma_e$ is an ellipse, the Figure 14 shows case where the centre of ellipse is at zero hydrostatic stress. [9]

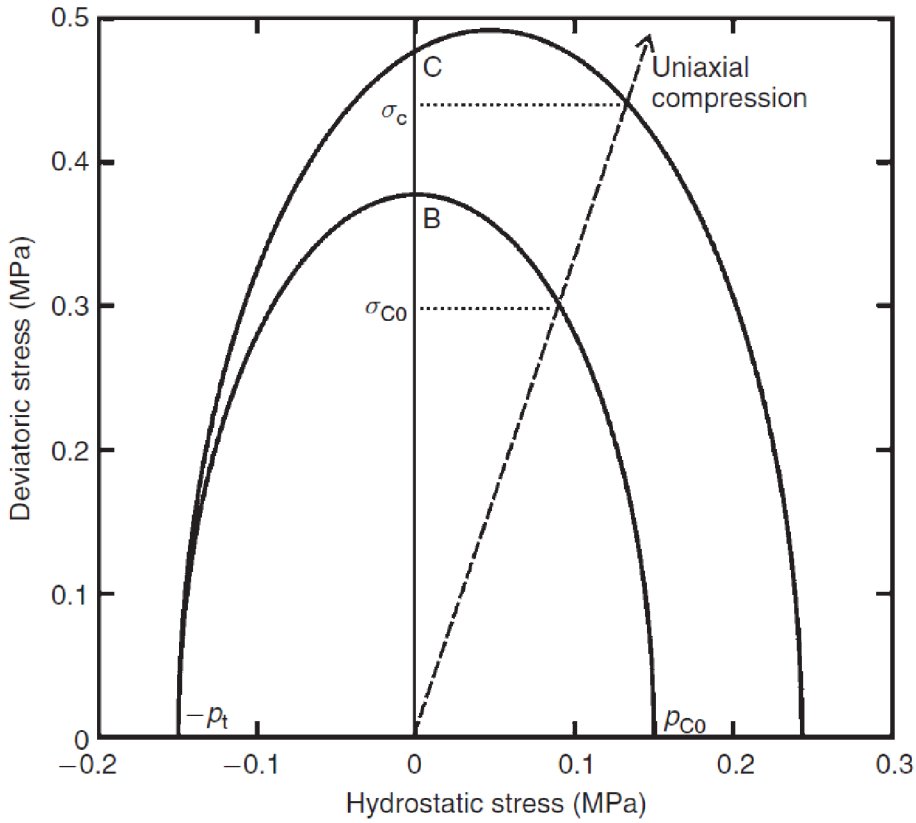


*Figure 14: Sections of the initial and hardened yield surface for XPS 35 foam, in the plane containing the hydrostatic axis. The surfaces have mirror symmetry about the horizontal axis. [9]*

- Initial yield:

  Values of three initial yield stresses determine the shape of the initial yield surface: Uniaxial compression $\sigma_{C0}$, hydrostatic compression $p_{C0}$ and hydrostatic tension.
- Hardening:

  Hardening is a function of the compressive inelastic volumetric strain $\varepsilon_{Vi}$ defined (7):

$$\varepsilon_V = -\ln\left(\frac{V}{V_0}\right) \tag{7}$$

  The model for uniaxial compression of closed-cell foam defines stress $\sigma_C$ as a function of engineering strain ε based on equation (8):

$$\sigma_C = \sigma_{C0} + \frac{p_0\varepsilon}{1 - \varepsilon - R} \tag{8}$$

where $\sigma_{C0}$ is the initial yield stress, $R$ is the foam relative density, and $p_0$ is the effective absolute gas pressure in the undeformed cells. [9]

## 2.7. Crack growth in homogenous foams

To describe characteristic elastic stress field surrounding the crack tip on isotropic continuum materials the linear elastic fracture mechanics (LEFM) is used. The mean tensile stress $\bar{\sigma}$ (9) and maximum stress shear $\tau_{max}$ (10) for the mode I type of loading causing crack opening are defined in terms of polar coordinates as:

$$\bar{\sigma} \equiv \frac{\sigma_{xx} + \sigma_{yy}}{2} = \frac{K_1}{\sqrt{2\pi r}} \cos\frac{\theta}{2} \tag{9}$$

$$\tau_{max} = \sqrt{\left(\frac{\sigma_{xx} + \sigma_{yy}}{2}\right)^2 + \sigma_{xy}^2} = \frac{K_1}{2\sqrt{2\pi r}} \sin\theta \tag{10}$$

The scaling constant $K_I$ is called the stress intensity factor. The yield zone can be very close to the crack tip and surrounded by LEFM stress field. A crack will grow only if the stress intensity factor $K_I$ is larger than the fracture toughness $K_{IC}$ of the material. If the fracture can be described by LEFM, $K_{IC}$ should be independent of the crack length, the fracture surface should be flat on a macro-scale, and crack propagation should be at a high speed. [9]

### 2.7.1. Fracture toughness of open-cell foams

There is a regular hexagonal honeycomb model under tension in the plane of the cells proposed (Figure 15). This model may be appropriate for ceramic and metal open-cell foams, but there is a discussion about its use for open-cell PU foams, because originally there is assumed that the crack tip is located at the middle of single cell. It has been said that this assumption is wrong, because crack tip would appear at the edge the cell. Modelling of fracture toughness of open-cell foams isn´t fully done yet. [9]

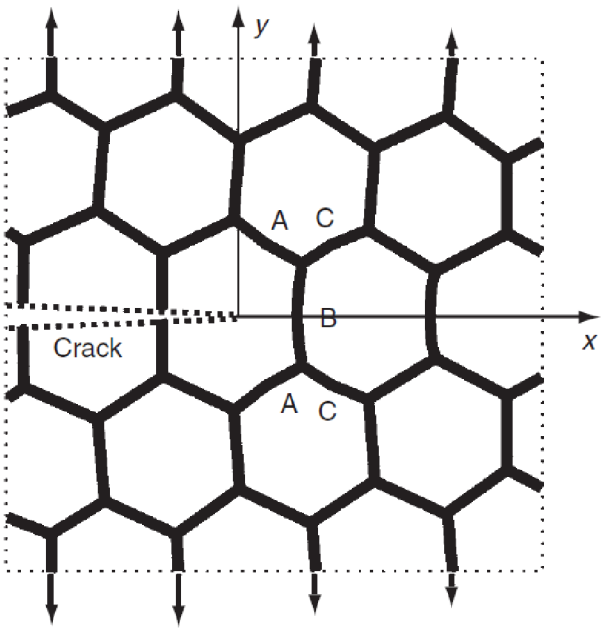


*Figure 15: Region around a crack tip in a loaded honeycomb. [9]*

### 2.7.2. Fracture toughness of thermoplastic foams

Research found linear relationship between $K_{IC}$ and foam density in the interval 60–200(300) kg · m$^{-3}$, at higher densities when the microstructure doesn´t consist of polyhedral cells, the relationship becomes non-linear (Figure 16). Results show different top limit of interval, probably due to the different foam tested. Rigid closed-cell PU foams, brittle polymethacrylimide closed-cell foams and Divinyllcell H200 PVC foams were measured. The specimen design also affected test results due to the different crack growth directions in the anisotropic foam. [9]

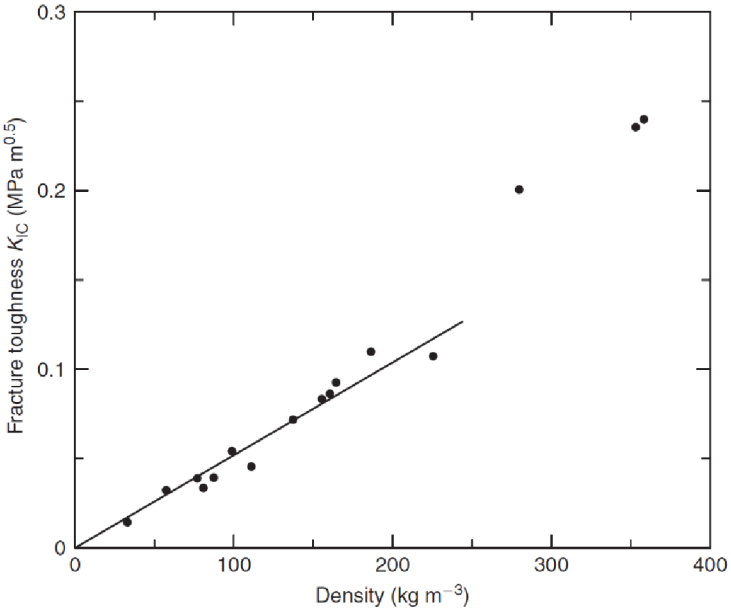


*Figure 16: $K_{IC}$ vs. density for rigid PU foams. [9]*

## 2.8. Effect of pore geometry

Mechanical properties of porous materials depend on the ratio of the sample size to the cell size and diameter. It is common to have components consisting of only a few cells, considering cell size in many engineering materials is from 1 to 10 mm. Therefore, it is important to understand the link between cellular morphology and size effects in terms of mechanical testing and designing of a material. [29, 30]

The mechanical behaviour depends on relative density, the properties of the cell wall material and the cell geometry. Also, it is important to take in consideration location of cells, cell in the bulk, surrounded by other cells responses differently than cell located near the edge, where kinematic boundary conditions are applied. If all dimensions of foam sample are large enough to include many cells, the differences average out. However, if one of the structural dimensions contains only a few cells mechanical properties depends on a size on this dimension. Experiments show that the bending and torsional rigidities increase with decreasing sample size both for open and closed-cell foams. [29, 30]

Research shows that with size reduction of pores the most properties improves. Microcellular foams were then introduced, characterized by cell size of tens or hundreds of microns. Nowadays, nanocellular foams have been achieved with few polymers and represent a major research goal for plastics. Another interesting morphological feature that is the degree

of interconnectivity. Cell-wall opening mechanisms are today under consideration. If the bulk viscosity or the rigidity of the polymer is not sufficiently low, the cells that are nucleated may not grow much and the final morphology of the foam usually consists of isolated pores. If the cell number density is sufficient, and the viscosity of the medium permits cells to grow and impinge upon each other, there is the potential of forming an interconnected pore morphology. If, however, cells grow further they can coalesce and lead to large voids, leading to a nonuniform pore distribution and may display a bimodal morphology. Depending on application is desired pore morphology, while isolated pores are suitable for insulation applications, interconnected pores are better for sound insulation or biomedical scaffolds. [30]

# 3. AIM OF THESIS

The main goal of this master thesis is to confirm a hypothesis related to improvement of mechanical properties of functionally graded foams. As a comparison regular foams were used. Secondary goal is designing of a preparation technique leading to formation of functionally graded structure.

# 4. EXPERIMENTAL PART

## 4.1. Chemicals

Below is a list of used chemicals and materials for experimental part of this thesis:

- Toluene p.a. (Lach-Ner s. r. o.)
- Tetrahydrofuran p.a. (THF; Penta s. r. o.)
- Polystyrene Krasten 154 (Synthos a. s.)
- Citric acid anhydrous (Penta s. r. o.)
- Dibenzoyl peroxide paste (Norpol, Reichhold)
- Styrene (Lach-Ner s. r. o.)

## 4.2. Sample preparation

Characterization of raw materials was done at first place. Thermogravimetric analysis (TGA) of pure citric acid (appendix Figure 30) and PS (appendix Figure 31) and differential scanning calorimetry (DSC) of PS (appendix Figure 32) was done. According to results of TGA the temperature of decomposition of citric acid is 178 °C, which would be ideal temperature for sample foaming, because PS decomposition starts at 250 °C (TGA) and glass transition temperature ($T_g$) of PS is 88 °C (DSC).

### 4.2.1. Solvent evaporation technique

20 g of PS was dissolved in 50 ml of THF. As a solvent, toluene was also used, but it was found out that evaporation is more difficult (appendix Figure 33) and THF is more suitable solvent, because of the ability of a citric acid to dissolve in a THF on the contrary of toluene. 1–4 wt. % of citric acid was added as a blowing agent, stirred and dispersed with ultrasonic homogenizer to obtain homogeneous mixture. The mixture was then spread into thin layer with approximately 2 mm height and it was left for 36 h in a laboratory conditions to evaporate the solvent. TGA showed more than 10 wt. % (appendix Figure 34) of residual solvent after this time. Drying in a vacuum at 40 °C for 96 h was done with the aim of reducing an amount of residual solvent below 1 wt. % (appendix Figure 35). PS sheet was cut into suitable pieces and placed into a preheated die. Sample was foamed at 180 °C for 10 min and after foaming, the sample was let to cool at laboratory temperature.

### 4.2.2. Solvent polymerization technique

20 g of PS was dissolved in 50 ml of styrene. Then a citric acid in an amount ranging from 1 to 4 wt. % was added as a blowing agent and 1 wt. % of dibenzoyl peroxide paste was added as an initiator. The mixture was stirred and homogenized using an ultrasonic homogenizer to disperse citric acid as homogenously as possible. This mixture was poured into a die and heated to 110 °C for 1.5 h to polymerize styrene. Samples with 2 mm height were prepared this way with different amount of a citric acid. A laminate with different amount of blowing agent in each layer was prepared. First layer contained 0 wt. % of blowing agent, second 4 wt. % and third layer 2 wt. % blowing agent. This order was chosen with a goal to prepare structure with pore size gradient. First layer without any pores and the third one with large pores. A citric acid acts also as a nucleation agent, thus the order of layers. This laminate was

placed into a die, heated to 215 °C for 10 min and foamed. The temperature was chosen according to TGA results, which showed decomposition temperature of blowing agent in this system at 213.42 °C (appendix Figure 36). Then were samples cooled at room temperature.

## 4.3. Test methods

The following chapters provide information about parameters of testing methods, which were used in this diploma thesis.

### 4.3.1. Thermogravimetric analysis

TGA was used for characterization of raw materials and intermediate products using Perkin Elmer TGA6 instrument. TGA of raw materials determined decomposition temperatures, testing parameters were set: heating 10 °C · min$^{-1}$ to 550 °C for citric acid and PS sheet in inert atmosphere of nitrogen, then isothermal for 5 min in oxidizing atmosphere of air in order to decompose residues non-flammable in nitrogen.

Maximum temperature for PS granulate was set to 600 °C, otherwise, parameters did not change.

TGA of intermediate products was done with purpose to determine either amount of residual solvents or the decomposition temperature of citric acid in certain system. Testing parameters were same as for raw materials with different maximum temperature, which was set to 450 °C, because the higher temperature wasn.t necessary.

### 4.3.2. Differential scanning calorimetry

DSC was done for determination of $T_g$ of PS Krasten 154 granulate, testing parameters were set: heating 10 °C · min$^{-1}$ up to 200 °C in inert atmosphere of nitrogen, gas flow 70 ml · min$^{-1}$, air cooling after analysis. Analysis was performed using TA instruments Calorimeter.

### 4.3.3. Optical microscopy

For morphology examination of prepared sample an optical microscopy (OM) was used via direct polarization microscope BX 50 and picture were shot using camera Olympus connected to the instrument.

### 4.3.4. Flexural test

Flexural test was performed in order to compare mechanical properties of functionally graded samples with regularly foamed samples. Zwick Z010 instrument was used for this analysis. Parameters of test: three-point bending geometry, measuring head with 10 kN maximum load, support separation 96 mm, diameter of support and load grips 5 mm, test speed 5 mm · min$^{-1}$. Testing samples had rectangle cross-section with dimensions of 15×8×120 mm. Parameters of test were set as specified in ČSN EN ISO 178 except the dimensions of samples, which had bigger height than the standard specifies, because of the difficulties with preparation of samples with specified dimensions. Values of strength and elastic modulus were calculated from results of 5 samples in all series.

Strength $\sigma$ of samples was calculated according formula (11):

$$\sigma = \frac{3FL}{2bh^2} \tag{11}$$

where $F$ is loading force (N), $L$ is support separation (mm), $b$ is width of a sample (mm) and $h$ is height of a sample (mm). Deformation $\varepsilon$ was calculated according to (12):

$$\varepsilon_i = \frac{6 s_i h}{L^2} \tag{12}$$

parameter $s_i$ stands for a certain deflection of a sample (mm). Elastic modulus $E$ (MPa) was calculated according to (13):

$$E = \frac{\sigma_{f_2} - \sigma_{f_1}}{\varepsilon_{f_2} - \varepsilon_{f_1}} \tag{13}$$

All equations are used according to standard ČSN EN ISO 178.

#### 4.3.5. Impact test

The impact strength was tested with the same purpose as flexural test, therefore, for the comparison of functionally graded and regular foams. Pendulum hammer Zwick was used for this analysis. Test was performed using hammer with parameters: 451.1 g weight, 2.7 J energy and 3.46 $m \cdot s^{-1}$ falling speed, support separation of samples was 40 mm and dimensions of testing samples were 15×8×60 mm. Impact strength $A$ ($kJ \cdot m^{-2}$) was calculated according to (14):

$$A = \frac{E_c}{hb} \cdot 10^3 \tag{14}$$

where $E_c$ stands for energy used for breaking a sample (J). Equation is used according to standard ČSN EN ISO 179-1. Values of impact strength were calculated from results of 5 samples in each series.

# 5. RESULTS AND DISCUSSION

## 5.1. Solvent evaporation technique

It was found out that solvent evaporation technique is unsuitable for preparation of functionally graded foams. Even after evaporation of more than 99 wt. % of solvent, a partial physical foaming occurred, which caused coalescence of foam cells and collapsing of structure in a cooling process. This can be seen in the picture of the sample in the Figure 17. Where, mainly in the middle of a sample, is large space created by coalescing of cells.

Many attempts of optimizing this technique were done. Mainly, use of different die geometries were tried, but with little or no success. Therefore, mechanical testing was not performed on samples prepared this way and any further research was done using solvent polymerization technique.

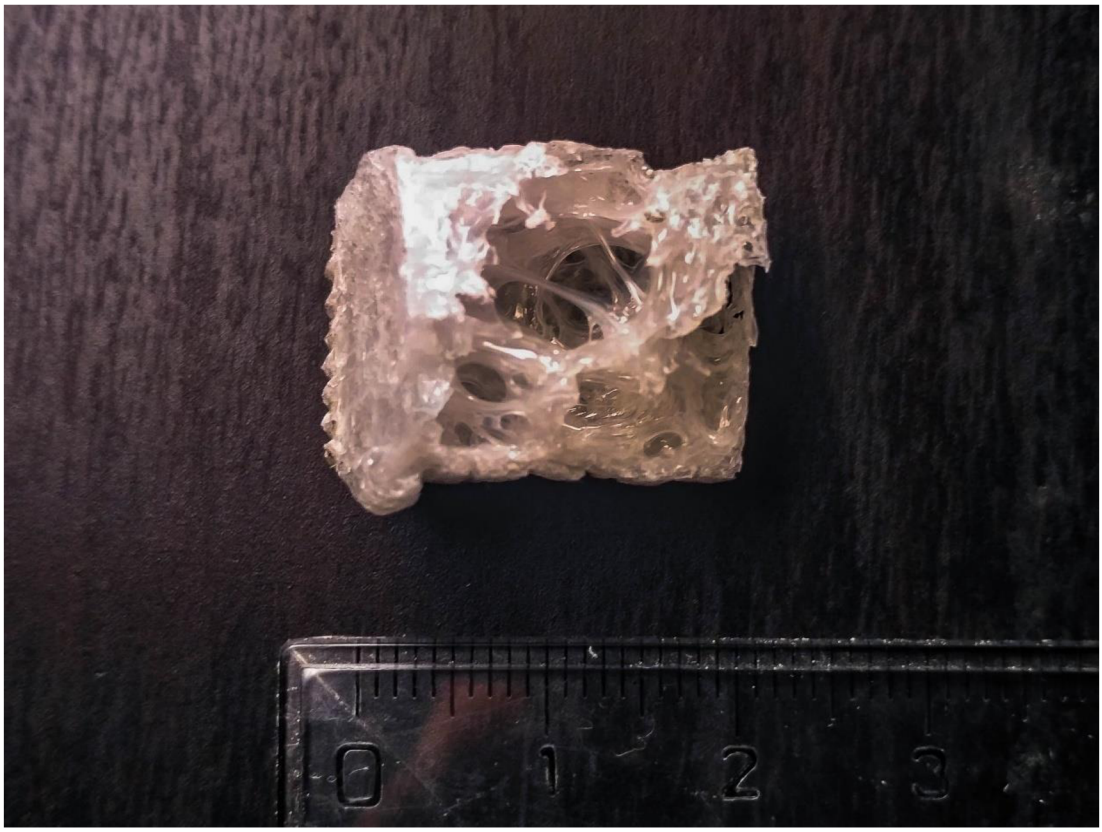


*Figure 17: Photograph of fracture cross-section of a sample prepared with solvent evaporation technique, THF used as the solvent.*

## 5.2. Solvent polymerization technique

Due to the polymerization of a solvent, there was no occurrence of a physical foaming in this sample preparation technique. Prepared structure was more homogeneous than in the previous technique. However, if foaming time was not respected, coalescence of cells appeared due to a high foaming temperature. Morphology examination, via optical microscope, was performed, therefore, images of sample are in following chapters (5.2.1). Testing and comparison of mechanical properties with regular foam was performed.

### 5.2.1. Morphology examination

Examination of foamed structure was performed via OM on a fracture area of prepared sample. In the following pictures, there is a comparison of cell size with direction from the top of the sample to the bottom. The top layer contains 0 wt. % of blowing agent, middle layer contains 4 wt. % of blowing agent and bottom layer 2 wt. %. Higher amount of a blowing agent causes creation of more nucleating sites, which causes formation of smaller cells. That was the reason of application of this gradient into the structure. That correlated with the aim of this thesis which was obtaining structure with increase of a pore size in one direction.

Figure 18 displays a cell structure at the top of the sample. Cell size of observed cell is $58.9 \cdot 10^3$ $\mu m^2$. Prepared foam has an open-cell structure, which can be observed also in following pictures. There is also comparison of cell size. In process of foaming, gas created by decomposition of a blowing agent is trying to escape from a bulk of the sample. Higher temperature of PS causes its low viscosity and escaping bubbles of gas have less resistance. Bubbles than go through the mass of PS melt and gets closer to the surface. Therefore, foaming properties must be set precisely.

In the Figure 19, there is an image of the same sample as in the Figure 18. The picture is taken from a middle of the sample. Size of focused cell is 0.352 $\mu m^2$, which means the area of cells is getting larger with the direction to the bottom of the sample. Figure 20 focuses on the cell with area 0.912 $\mu m^2$, which is closer to the bottom of the sample. This observation confirms successful preparation of functionally graded foam structure.

An orientation of cells in horizontal lane can be observed. This was caused in process of foaming, when gas in a bottom of the sample expanded and tried to escape from the sample to the top. This caused upper cells to compress in a vertical plane. Another reason is slightly thinner sheets of PS than is size of a die and expansion of gas to sides of the sample had lower resistance. Samples were prepared thinner, than is the width of the die, so they can be easily put inside.

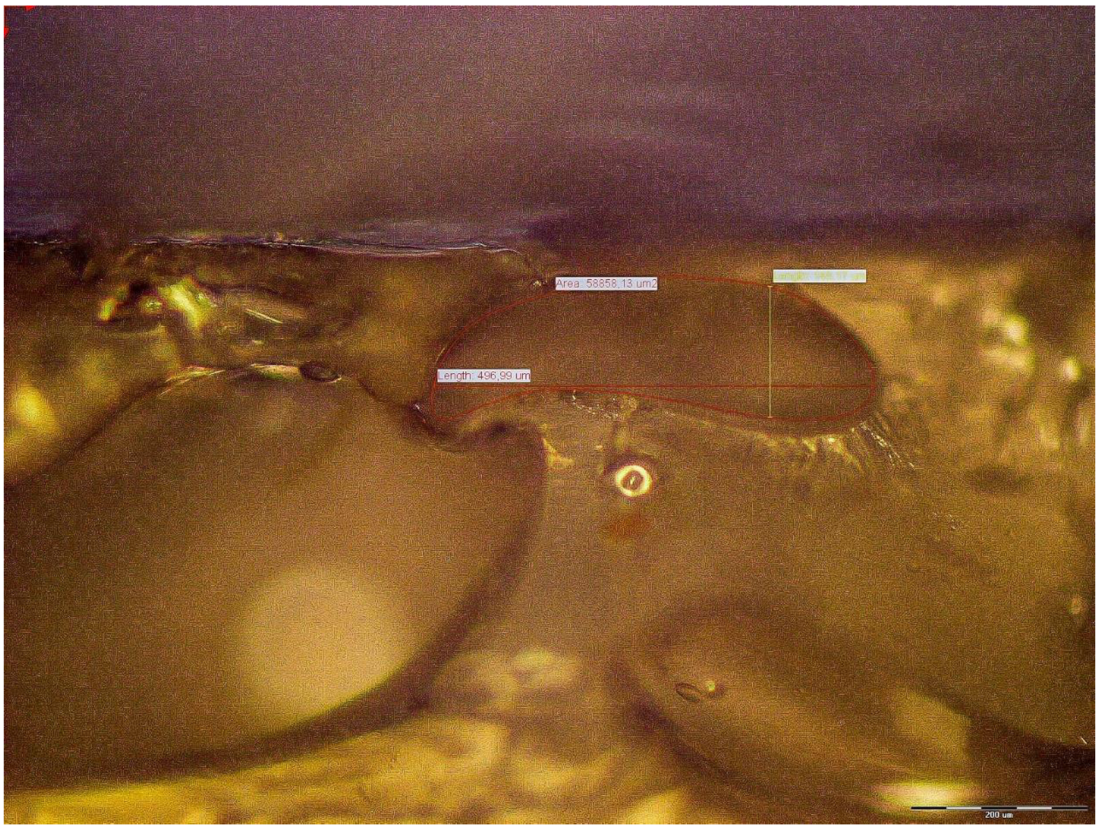


*Figure 18: Image of cell structure of functionally graded foam, size of cell is 58.9 · $10^3$ $\mu m^2$, scale bar is 200 $\mu m$; OM.*

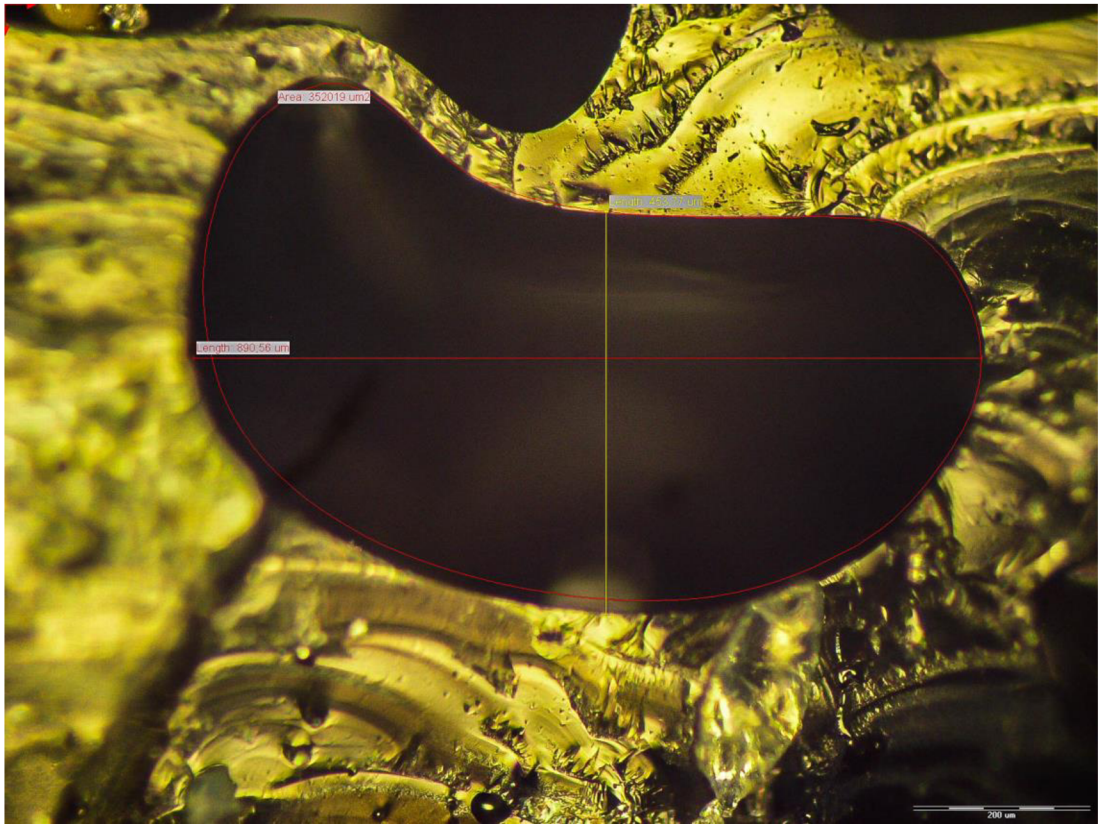


*Figure 19: Image of cell structure of functionally graded foam, size of cell is 0.352 $\mu m^2$, scale bar is 200 $\mu m$; OM.*

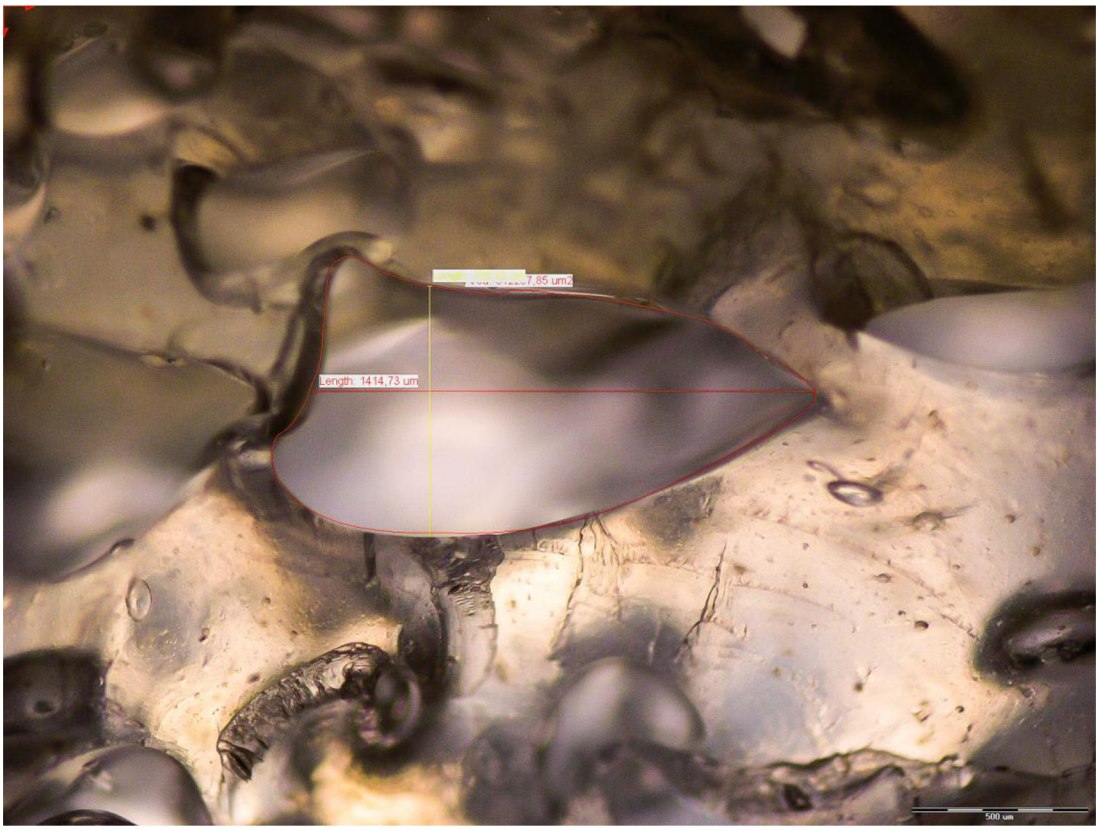


*Figure 20: Image of cell structure of functionally graded foam, size of cell is 0.912 μm$^2$; scale bar is 500 μm; OM.*

### 5.2.2. Testing of mechanical properties

Flexural bending test and impact test were performed with purpose of comparison of a regularly foamed structure with functionally graded foams. 5 series with different densities were prepared as a reference for functionally graded samples. Compared properties were elastic modulus, strength and impact strength of a material. Samples with the highest density were compact. With decreasing density, samples were foamed with 1, 2, 3 or 4 wt. % amount of a blowing agent, respectively.

Exponential increase of elastic modulus can be observed with increasing density of samples, which is an effect of a foamed structure. With lower density higher amount of a blowing agent was used, which caused creation of higher number of cells.

However, elastic modulus and strength of prepared samples did not achieve significantly better properties. Elastic modulus (Figure 21) of prepared sample is 870.12 MPa while estimated value established, on the basis of regression equation, was 1 098.19 MPa, which means that prepared sample has lower stiffness. Strength (Figure 22) of prepared sample is 5.96 MPa while estimated value is also 5.96 MPa, that means any significant improvement was not achieved in neither of parameters.

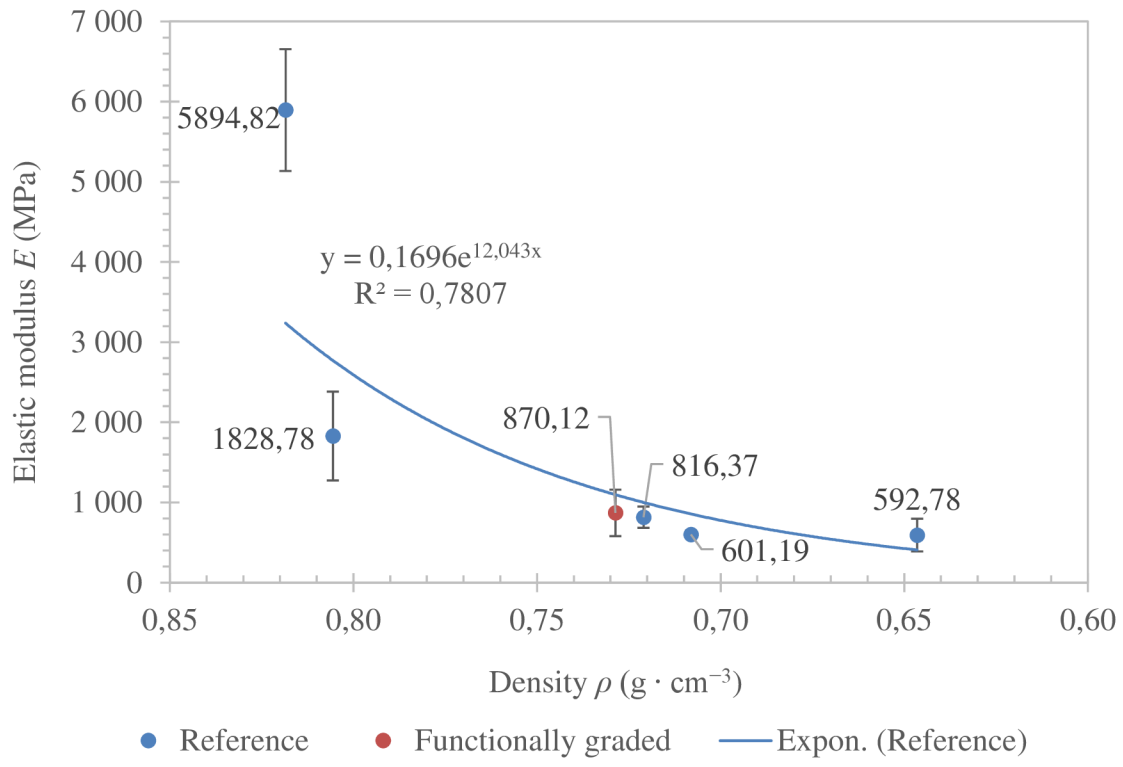


*Figure 21: Graph of an elastic modulus as a function of a density of foams, blue points are reference samples, red point stands for functionally graded sample and blue curve is regression equation.*

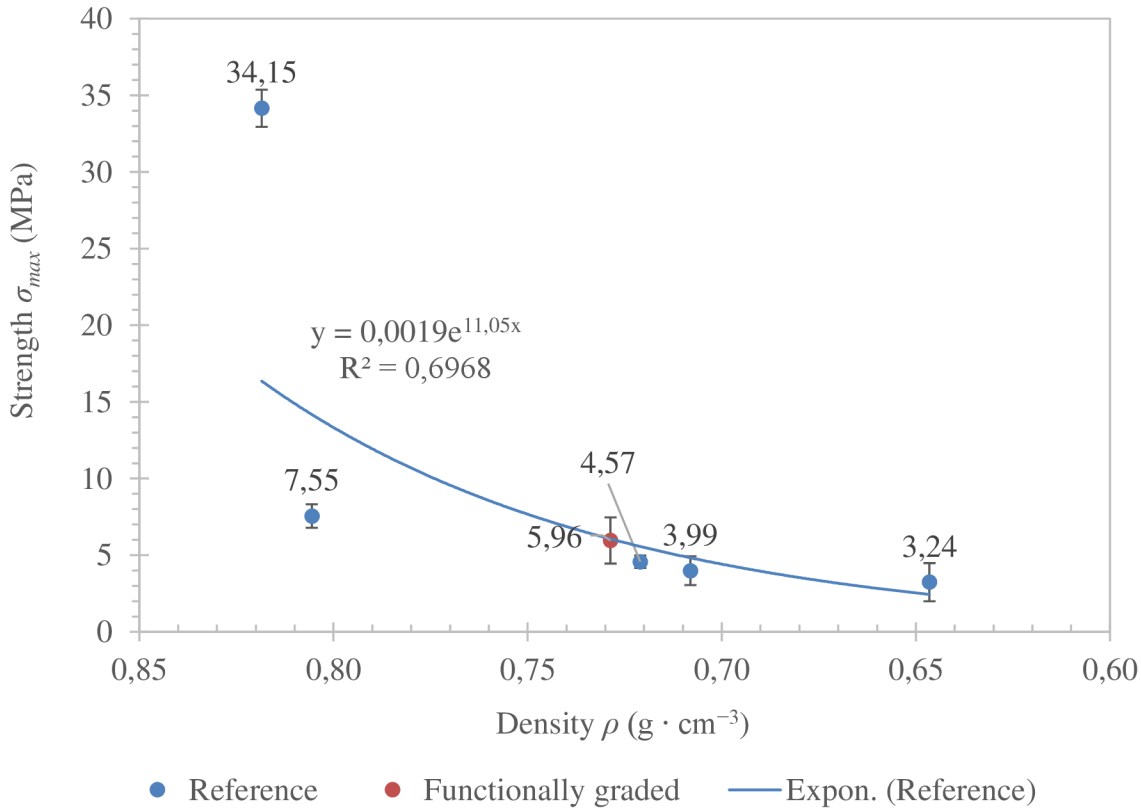


*Figure 22: Graph of a strength as a function of a density of foams, blue points are reference samples, red point stands for functionally graded sample and blue curve is regression equation.*

Impact strength (Figure 23) of functionally graded samples was significantly higher than impact strength of regular foams with the same density. Estimated value of impact strength, of regular foam with the same density as the functionally graded foam, is 0.686 kJ · m$^{-2}$, while real value of functionally graded sample is 0.940 kJ · m$^{-2}$.

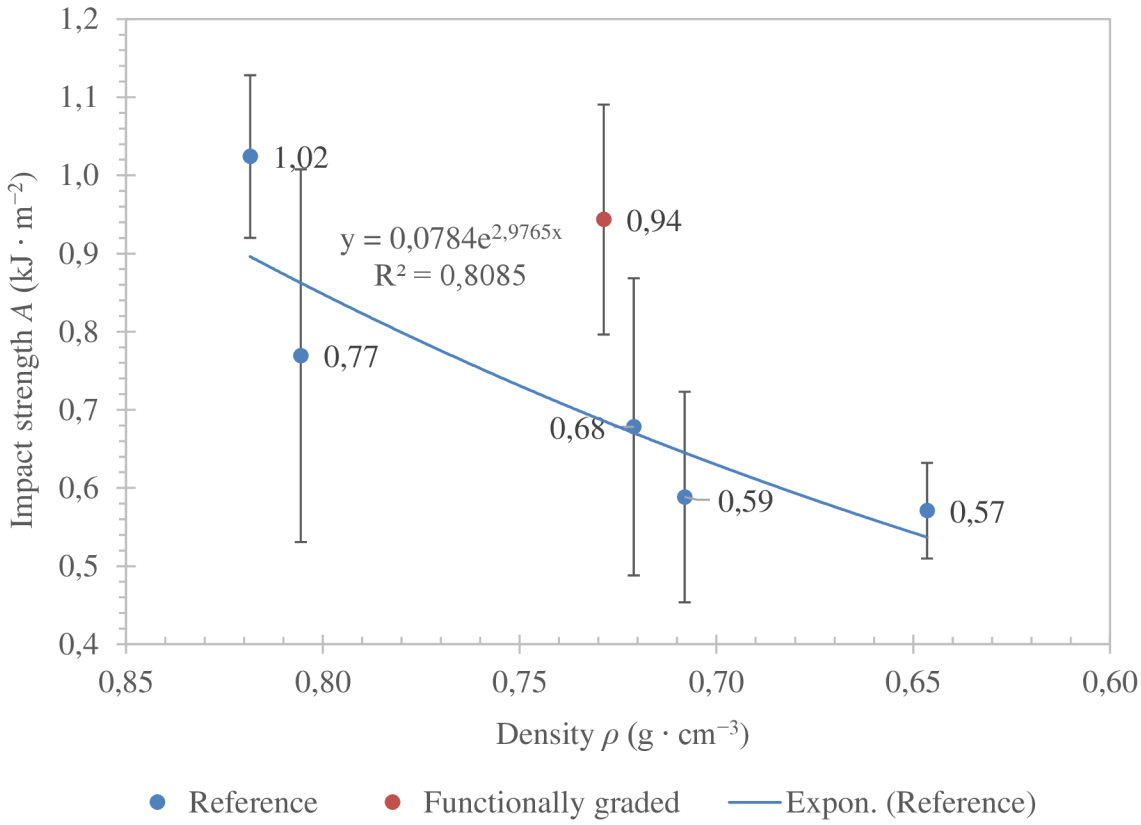


*Figure 23: Graph of an impact strength as a function of a density of foams, blue points are reference samples, red point stands for functionally graded sample and blue curve is regression equation*

All samples were very brittle, because of an absence of a plastic deformation. This can be observed in diagrams of flexural curve of samples (Figure 24; diagrams of reference samples stated in appendix Figure 37–Figure 41). The samples broke under certain amount of load without any signs of a plastic deformation. This was caused by properties of matrix used for sample preparation. PS is very brittle material, because of its amorphous structure. It was chosen as a suitable testing material for fundamental research of preparation of functionally graded foams. Further research should considerate use of other, probably semi-crystalline, polymer materials to achieve even better properties applicable also into industrial fields.

All results of mechanical testing are listed in Table 2 in an appendix.

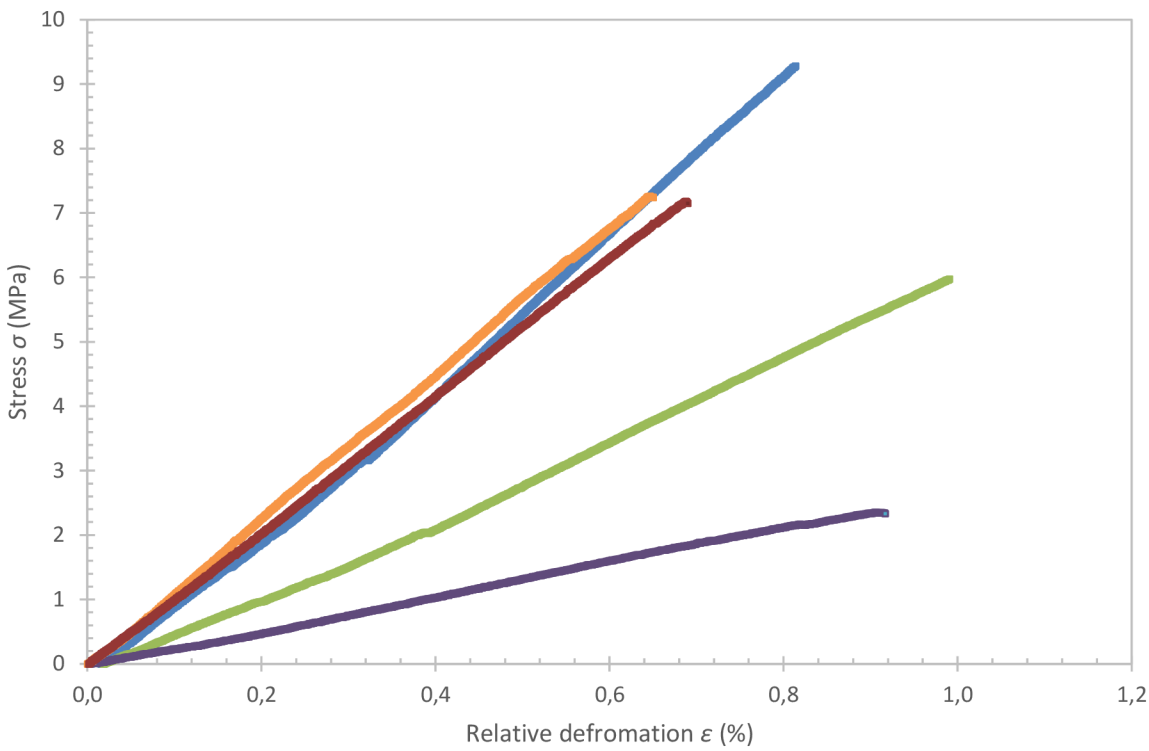


*Figure 24: Results of functionally graded samples, three-point bending flexural test display strain as a function of relative deformation.*

### 5.2.3. Comparison with theoretical models

Relative values of obtained results are compared to a model as presented by *M. F. Ashby* and *L. J. Gibson* in [31]. Both models, for relative elastic modulus and relative strength, are formulated for open-cell isotropic foams, with approximation of cell shape to a cubic array (Figure 25). It must be kept in mind that presented models are mentioned for ideal materials, while prepared samples have anisotropic structure with slightly oriented pores. Therefore, comparison of models won´t be fully accurate.

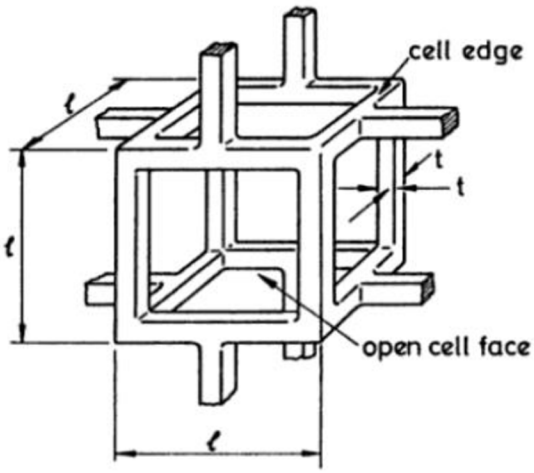


*Figure 25: Cubic model of an open-cell foam showing the edge length, l and the edge thickness, t. [31]*

Model was formulated for a relative elastic modulus $E^*/E_s$, where $E^*$ is elastic modulus of foamed sample with certain density $\rho^*$, and $E_s$ is an elastic modulus of a compact material with density $\rho_s$ (15):

$$\frac{E^*}{E_s} = \mathrm{C}\left(\frac{\rho^*}{\rho_s}\right)^2 \tag{15}$$

constant C includes all geometric constants of proportionality, C = 0.3. Red line in Figure 26 represents this theoretical model.

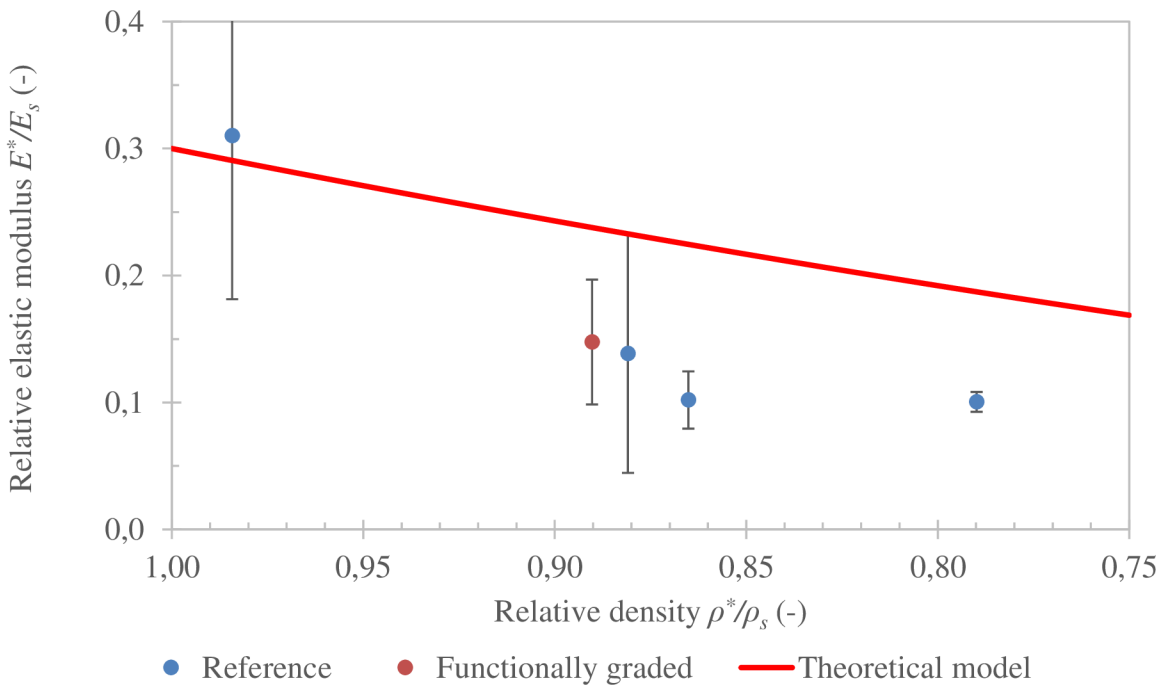


*Figure 26: Graph of a relative elastic modulus as a function of density, blue points represent reference samples, red line represents theoretical model and red point represents functionally graded sample.*

For relative strength of open-cell foam is defined similar theoretical model (16):

$$\frac{E^*}{E_s} = \mathrm{C}\left(\frac{\rho^*}{\rho_s}\right)^{3/2} \tag{16}$$

constant C = 0.3. Relative strength as a function of relative density is displayed in Figure 27, red line represents theoretical model.

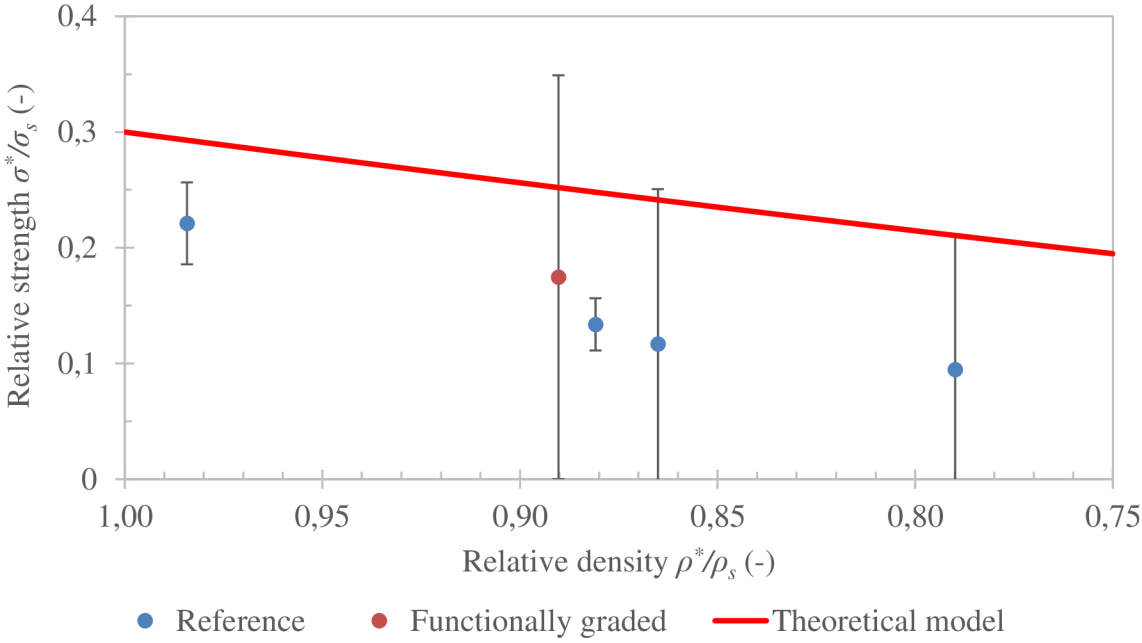


*Figure 27: Graph of a strength as a function of density, blue points represent reference samples, red line represents theoretical model and red point represents functionally graded sample.*

The obtained data achieve lower values than theoretical model suggests. This is caused due to the approximation of theoretical models in first place. Despite all efforts, prepared samples might contain some defects in their structure, which cause decrease of mechanical properties.

In compact material, resistance to crack growth is characterized as a plastic zone, which is defined by properties of the material. In foamed material, another aspect is brought into micromechanics of a material, which is moment of inertia. In macro scale, moment of inertia is defined by a shape and size of a sample and a direction of applied force with respect to a geometry of the sample. In foams, moment of inertia is defined for every cell, which is the reason of a preparation of functionally graded foams. Dependence of applied load ($F$) on moment of inertia ($I$) is described as (17) according to [32]:

$$F = 48\frac{EI\delta}{L^3} \tag{17}$$

δ stands for deflection (m), E is elastic modulus (Pa) and L is support separation (m).

With an increasing size of cells increases, also, a moment of inertia of these cells, while applied force stays constant. This slows crack growth speed and eventually stops it. Also prevents catastrophic fracture of the material. With correctly determined geometry of cells and gradient of cell size, properties of such foams can achieve higher level with the same density than foams with regular cell structure.

However, prepared functionally graded samples did not achieve expected improvement of mechanical properties, with exception of impact strength, neither in comparison to fitted data nor in comparison with theoretical models. This fact is probably caused by chosen geometry. Prepared functionally graded samples were asymmetric and loading force had to be applied on

the side of a sample with the largest cells (Figure 28). This could cause minor deformation of cells, in place of force application, and the process which was described above could not take place properly. Achieving of better properties is expected in case of symmetric samples with compact surfaces and symmetrically increasing size of cells with a direction to the centre of the sample (Figure 29). Force would be applied on compact surface of a sample and crushing of structure would be minimized. Unfortunately, samples with this geometry could not be prepared, because of complicated preparation method. Therefore, further research should be performed this way to achieve desired improvement of properties.

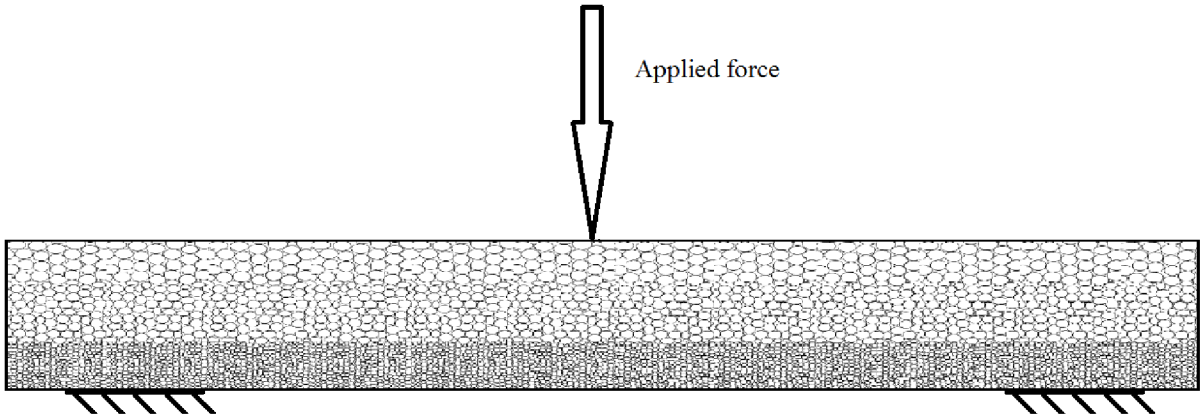


*Figure 28: Scheme of actual testing geometry of three-point bending test.*

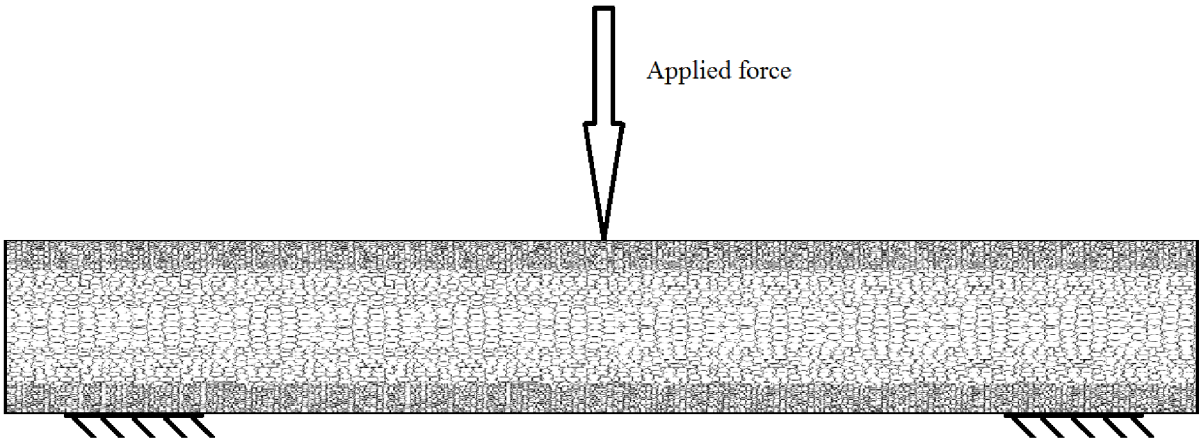


*Figure 29: Scheme of ideal testing geometry of three-point bending test.*

Improvement of impact strength was caused by described effect of gradient structure. The reason why this effect occurs only in terms of impact testing is because of application of dynamic stress on samples. High deformation rate of material causes sample to act more brittle than under lower deformation rate. Thus, the minor crushing of cells did not have enough time to occur and impact strength achieved higher level.

# 6. CONCLUSION

The main focus of this master thesis was functional polymer foams, specifically designing of preparation process of foams with a functionally graded structure. It was expected that these foams could obtain better mechanical properties with the same or a lower density as a regularly structured ones.

Preparation of functionally graded foam was achieved by dissolving PS in a reactive solvent, which was its own monomer - styrene. There were created thin sheets of PS with certain amount of a blowing agent, which were polymerized and fused together in a specific order at elevated temperature. Than the temperature was elevated in order of decomposition of the blowing agent and formation of foamed structure.

Successful preparation of functionally graded foam was examined via optical microscopy by comparing of cell structure and size throughout a bulk of the sample. It was confirmed that desired pore-size gradient was obtained using this process. Size of cells inside the sample was gradually increasing from the top to the bottom of the sample. Also, an orientation of cells was achieved due to foaming conditions. Thus, with introduced technique it is possible to prepare functionally graded foams even with oriented cells.

Three-point bending test and impact test were performed on prepared samples to compare their mechanical properties with regularly structured foams and state, if the designed geometry of pore-size gradient was efficient or not. Results of three-point bending test indicated slight improvement of properties in comparison with reference samples. Impact test indicated much better properties than reference samples, even that the prepared geometry of samples was not ideal.

Further research in this field should focus firstly on optimization of pore-size gradient, mainly on preparation of symmetric structures, which should provide even better results. Also, more focus on control over size and shape of cells is necessary, because it is also one of aspects which influences mechanical response of a material. And, last but not least, designing of preparation techniques of described foams from materials, which are more suitable for industrial application, such as semi-crystalline polymers.

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# 8. LIST OF ABBREVIATIONS

Abbreviations used in this thesis in order of their appearance in text.

| | |
|---|---|
| PU | Polyurethane |
| SEM | Scanning electron microscopy |
| LDPE | Low density polyethylene |
| PP | Polypropylene |
| PET | Polyethylene terephthalate |
| HDPE | High density polyethylene |
| PS | Polystyrene |
| PMMA | Polymethylmethacrylate |
| CBA | Chemical blowing agent |
| PBA | Physical blowing agent |
| RIM | Reaction injection molding |
| PLA | Polylactic acid |
| TIPS | Thermally induced phase separation |
| FEA | Finite element analysis |
| XPS | Extruded polystyrene |
| LEFM | Linear elastic fracture mechanics |
| PVC | Polyvinylchloride |
| TGA | Thermogravimetric analysis |
| DSC | Differential scanning calorimetry |
| THF | Tetrahydrofuran |
| OM | Optical microscope |

# 9. APPENDIX

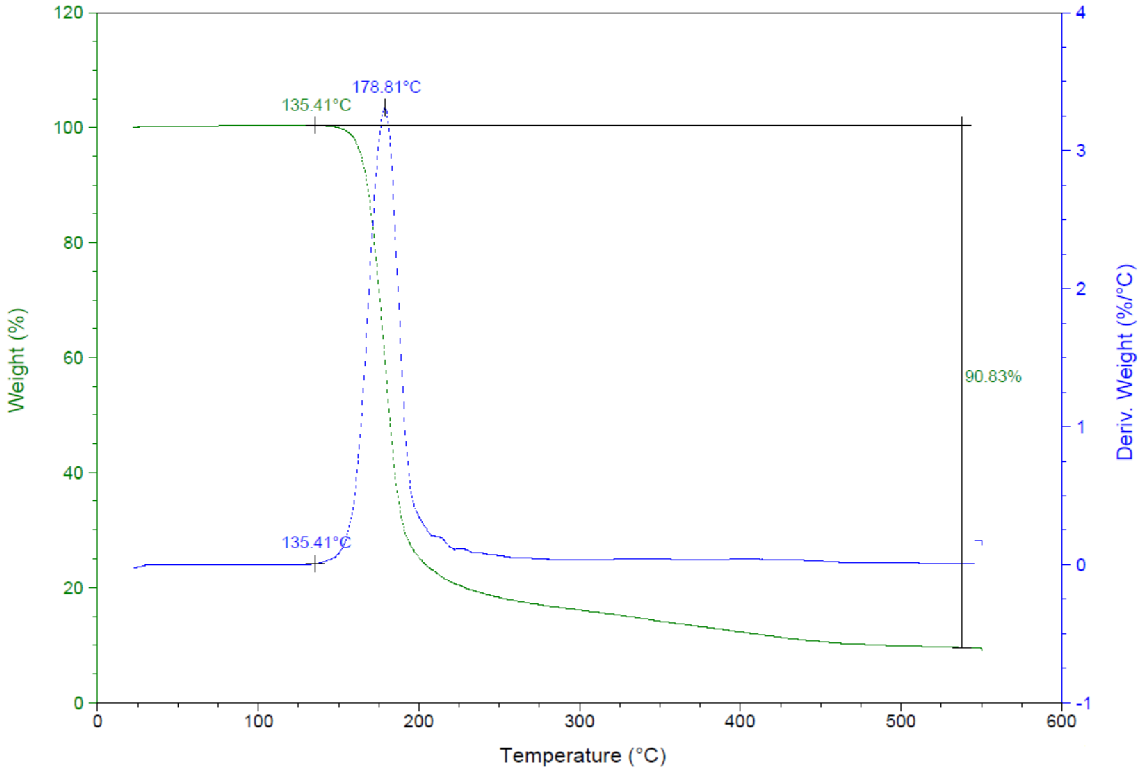


*Figure 30: TGA graph of a citric acid.*

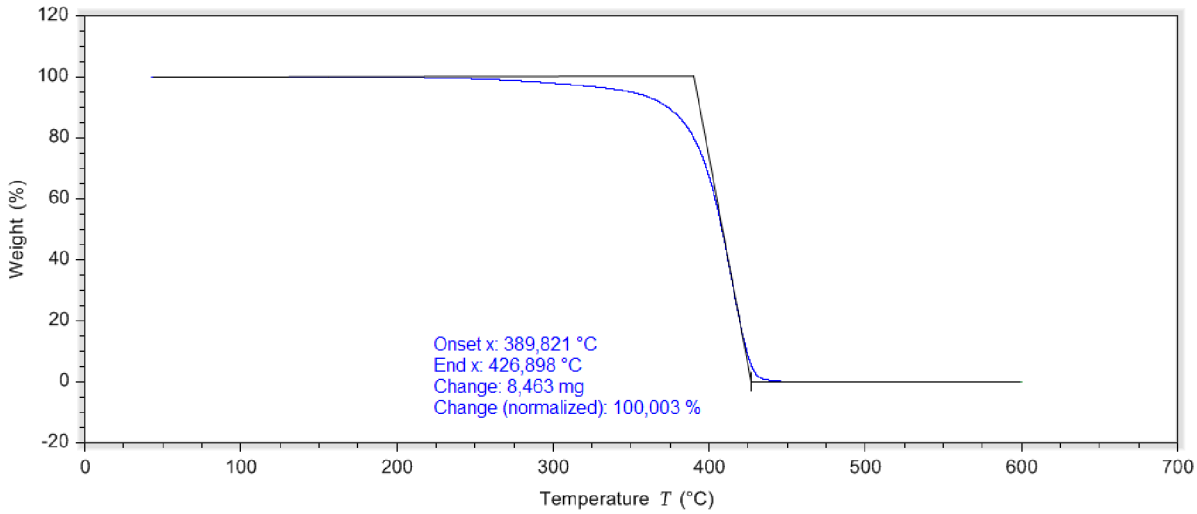


*Figure 31: TGA graph of a PS Krasten 154.*

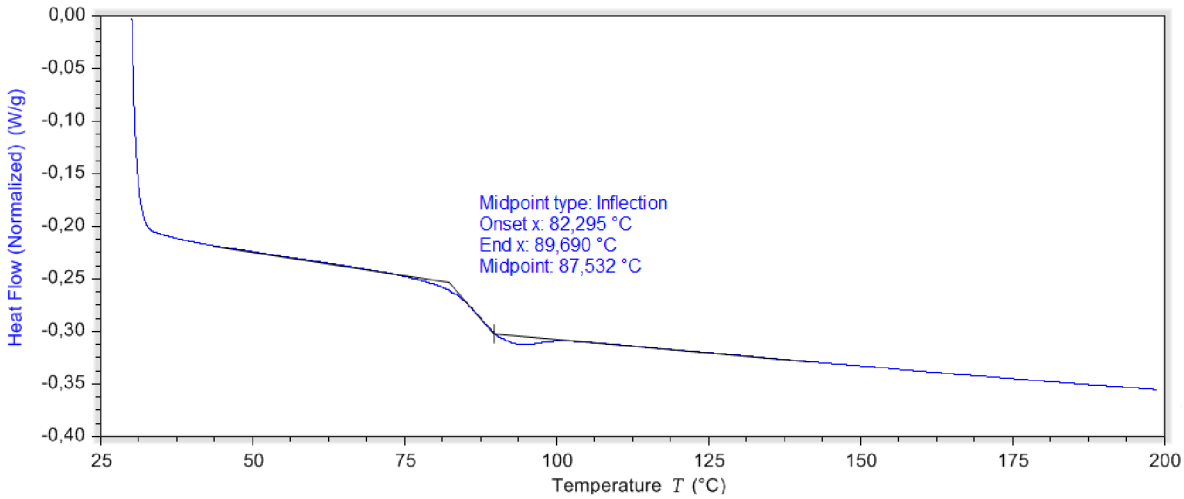


*Figure 32: DSC graph of a PS Krasten 154.*

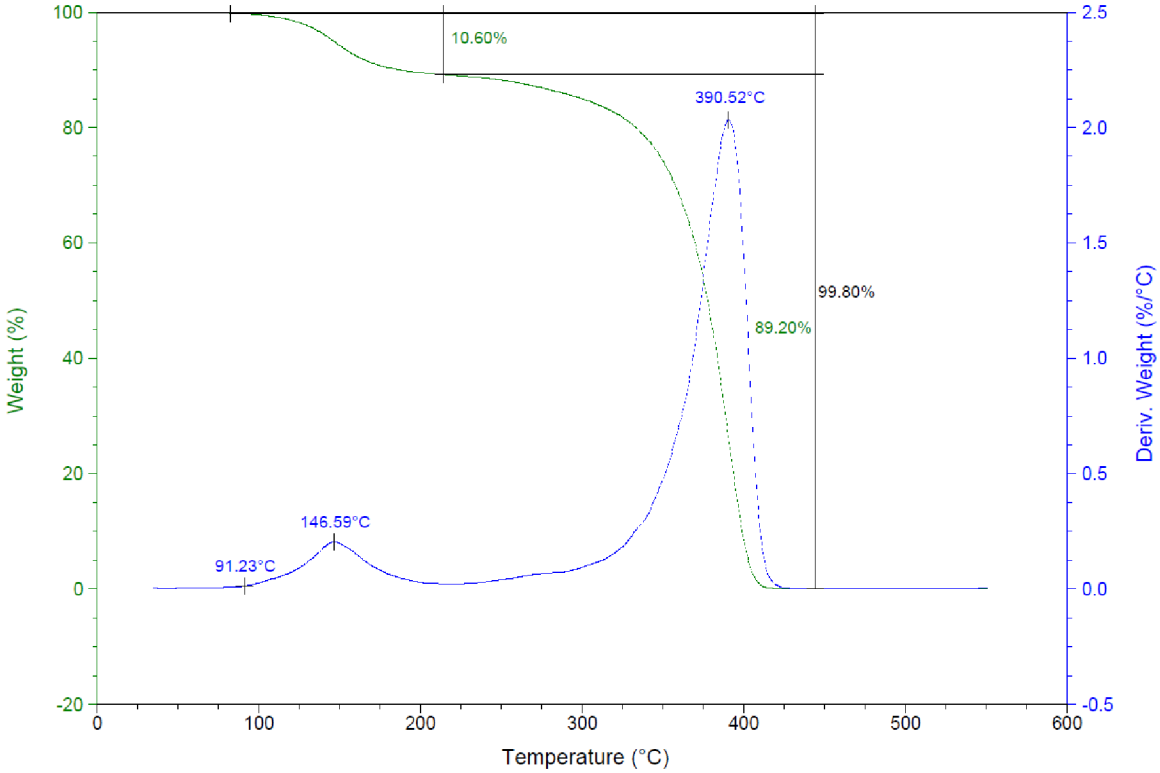


*Figure 33: TGA graph of a PS sheet with a residual solvent (Toluene).*

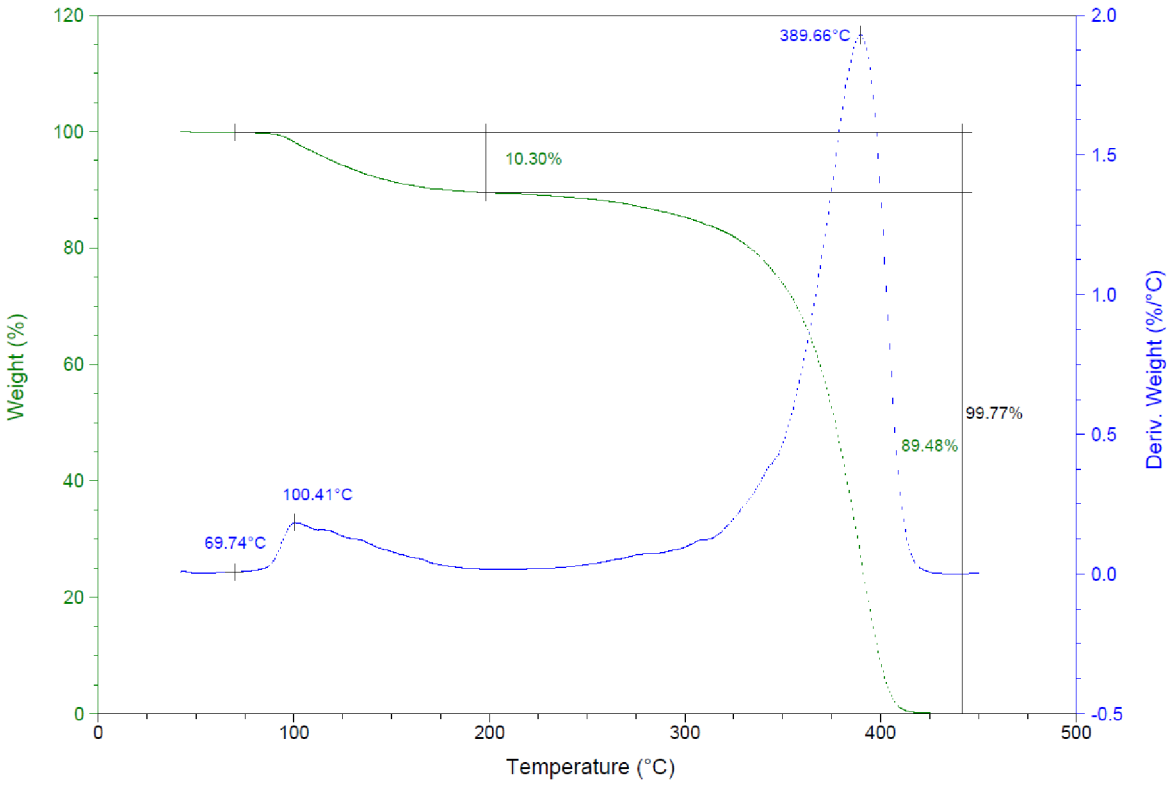


*Figure 34: TGA graph of PS sheet with a residual solvent (THF).*

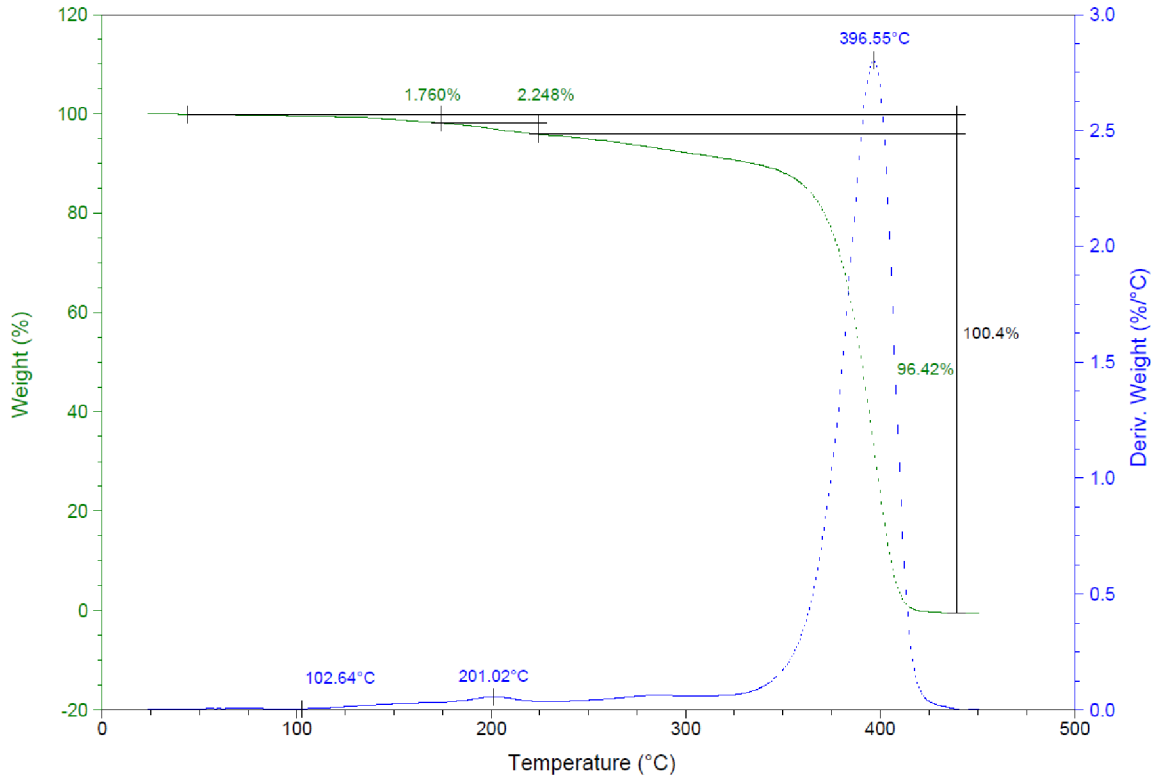


*Figure 35: TGA graph of PS sheet with a residual solvent (103 °C, THF) and a blowing agent (201 °C).*

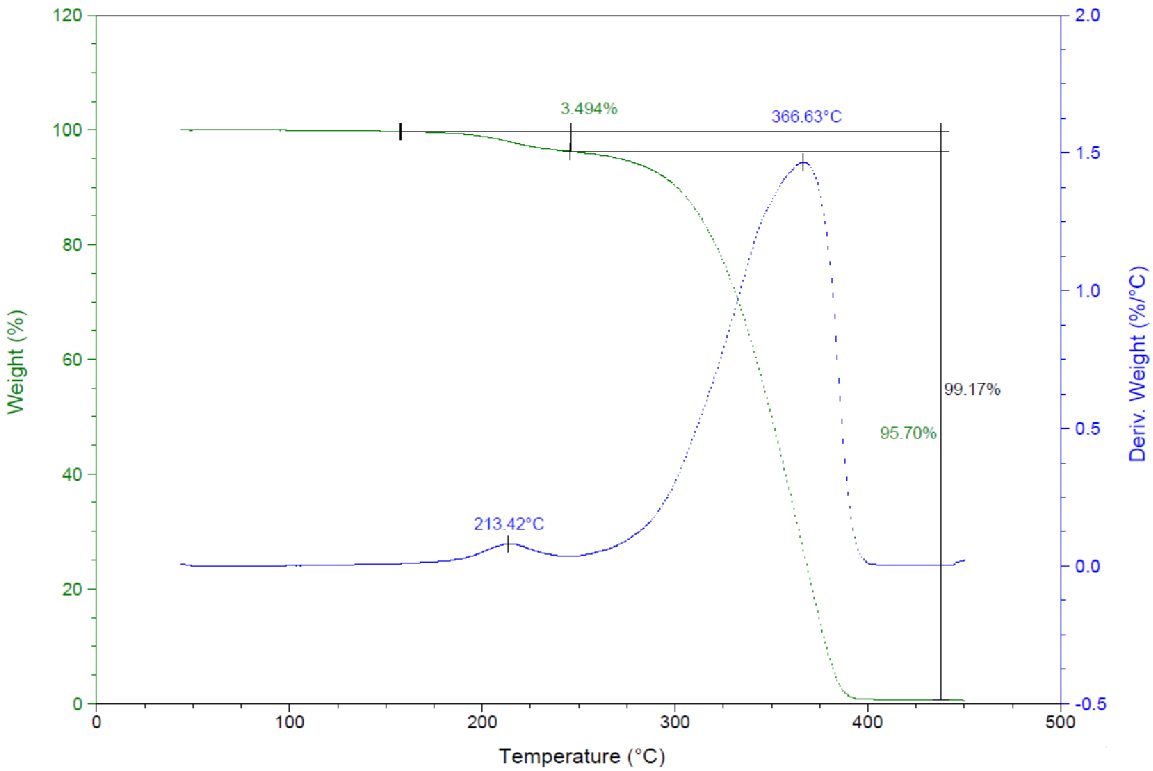


*Figure 36: TGA graph of PS sheet with a blowing agent (213.42 °C).*

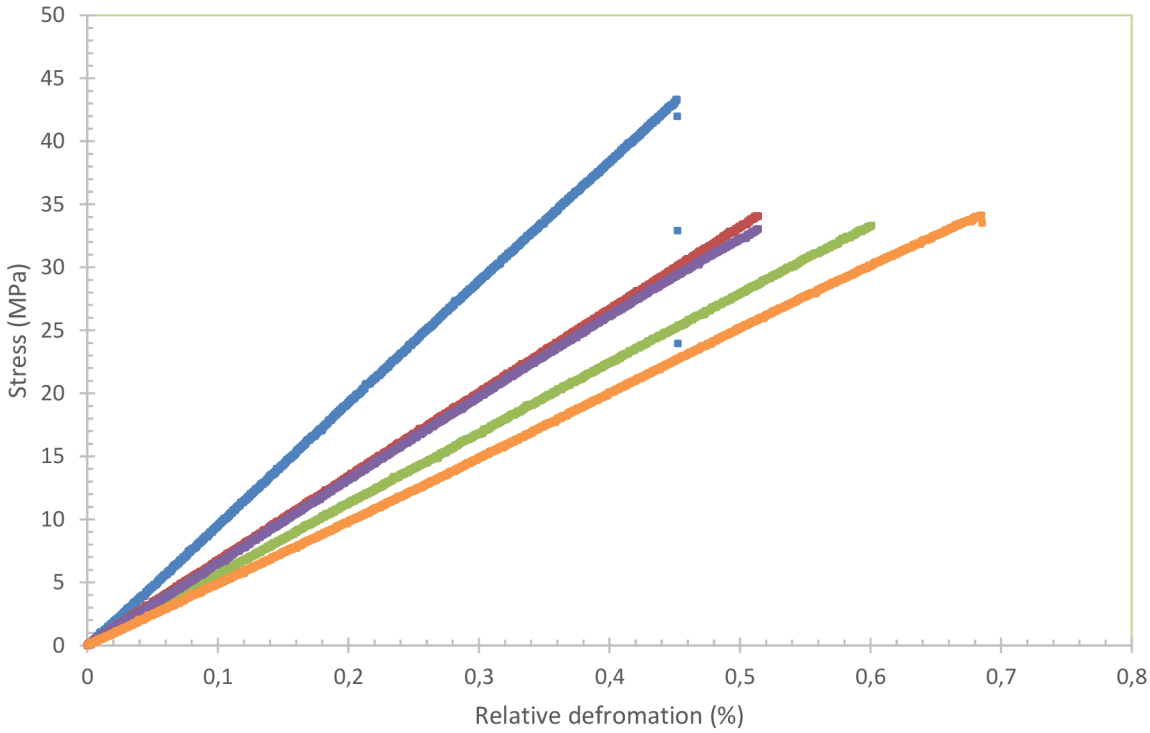


*Figure 37: Results of reference samples with 0 wt. % of a blowing agent, three-point bending flexural test display strain as a function of relative deformation.*

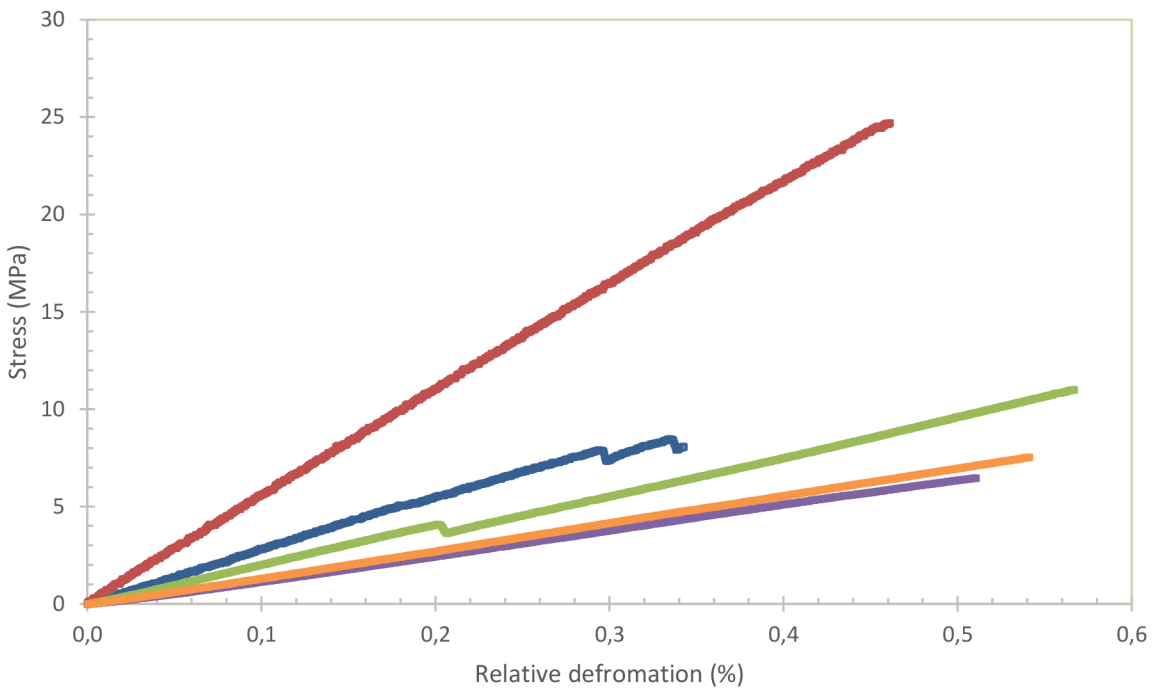


*Figure 38: Results of reference samples with 1 wt. % of a blowing agent, three-point bending flexural test display strain as a function of relative deformation.*

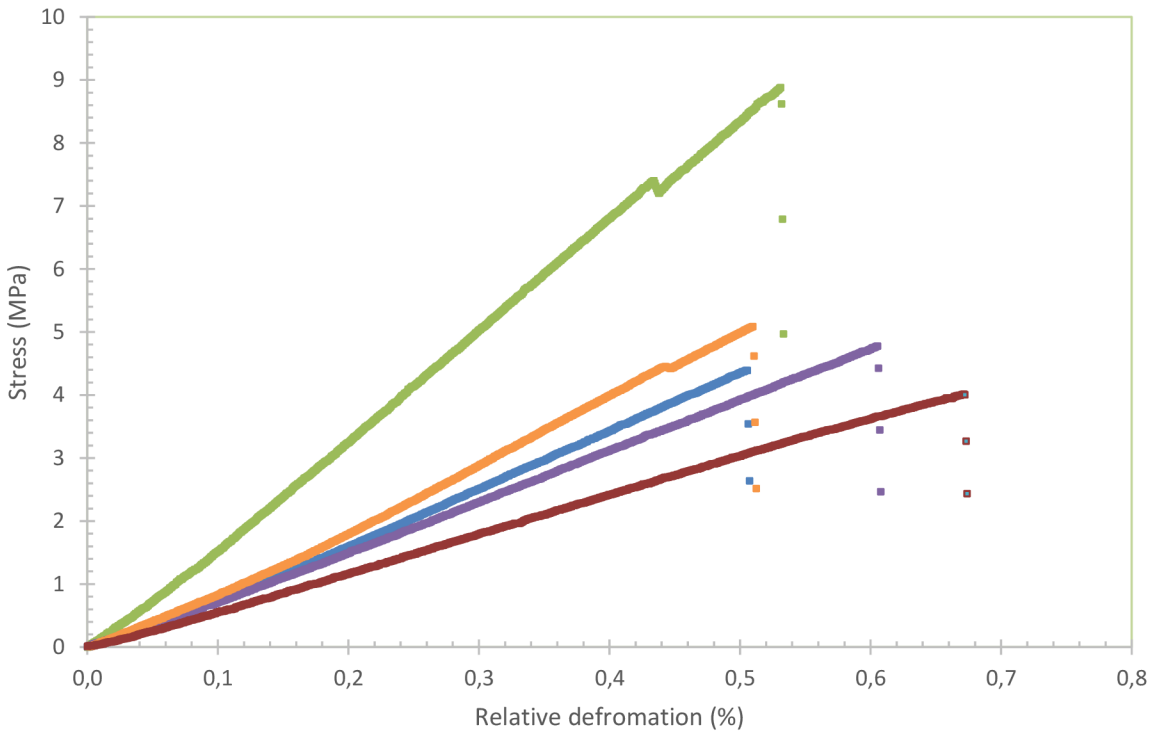


*Figure 39: Results of reference samples with 2 wt. % of a blowing agent, three-point bending flexural test display strain as a function of relative deformation.*

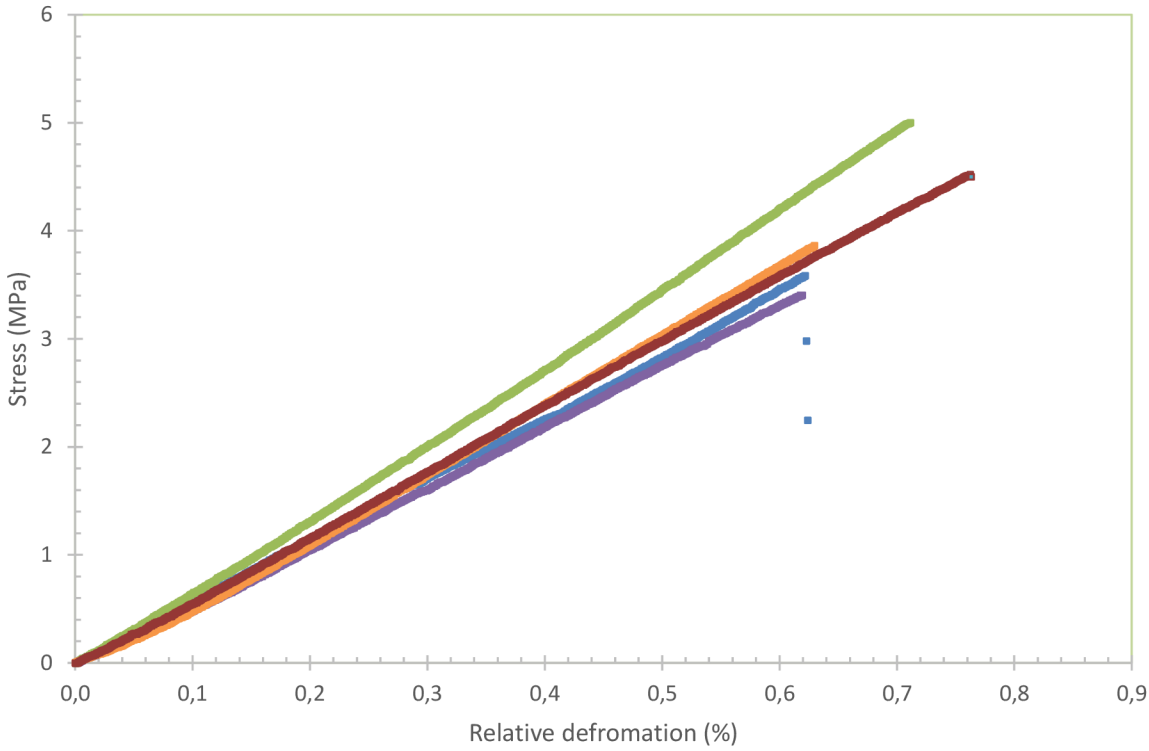


*Figure 40: Results of reference samples with 3 wt. % of a blowing agent, three-point bending flexural test display strain as a function of relative deformation.*

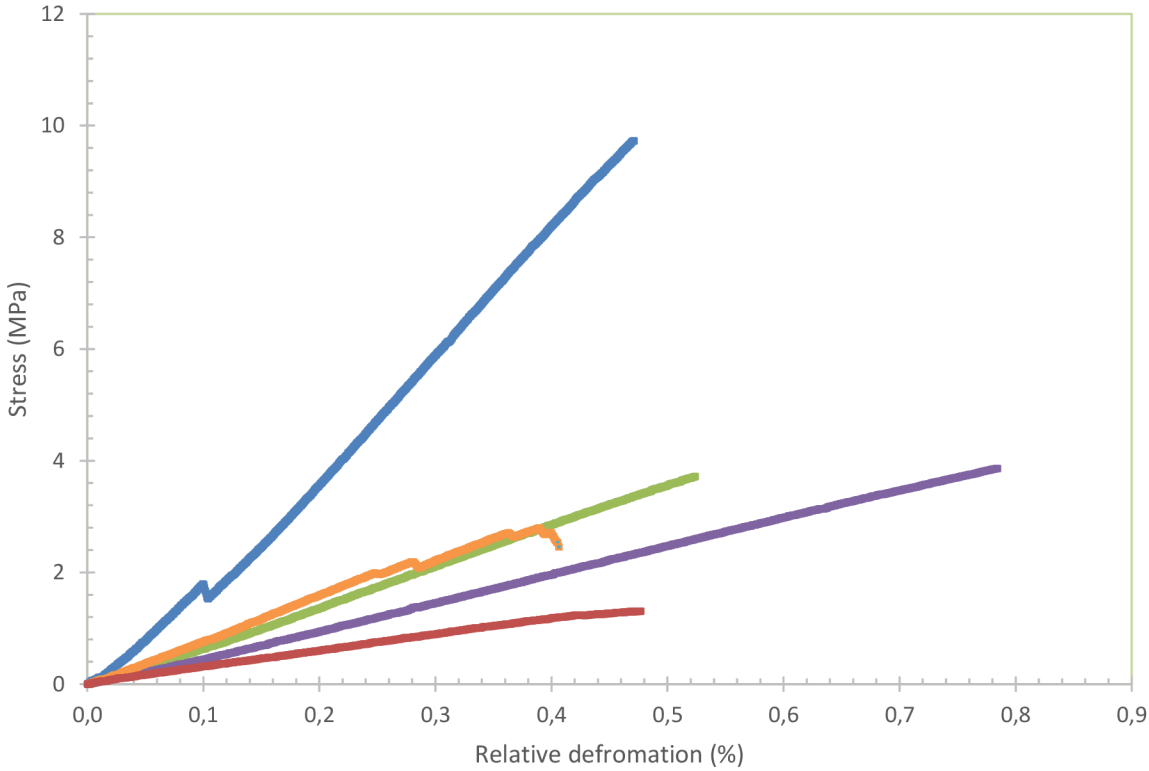


*Figure 41: Results of reference samples with 4 wt. % of a blowing agent, three-point bending flexural test display strain as a function of relative deformation.*

Table 2: Results of mechanical testing of reference samples (0–4 wt. %) and functionally graded samples (last lane).

| BA (wt. %) | Sample No. | E (J) | $F_{max}$ (N) | $\varepsilon(F_{max})$ (mm) | A ($kJ/m^2$) | $A_{avg}$ ($kJ/m^2$) | $A_{dev}$ ($kJ/m^2$) | $\sigma_{max}$ (MPa) | $\sigma_{avg}$ (MPa) | $\sigma_{dev}$ (MPa) | E (MPa) | $E_{avg}$ (MPa) | $E_{dev}$ (MPa) | ρ (g/cm3) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 0.038 | 20.19 | 3.70 | 0.956 | | | 34.09 | | | 6 701.50 | | | |
| | 2 | 0.048 | 22.90 | 2.98 | 1.193 | | | 33.32 | | | 5 584.43 | | | |
| 0 | 3 | 0.061 | 24.47 | 2.03 | 1.032 | 1.0 | 0.1 | 33.05 | 34.2 | 1.2 | 6 646.17 | 5 895 | 760 | 0.82 |
| | 4 | 0.045 | 30.71 | 3.60 | 1.015 | | | 34.14 | | | 5 601.89 | | | |
| | 5 | 0.039 | 35.35 | 2.01 | 0.924 | | | 36.14 | | | 4 940.09 | | | |
| | 1 | 0.030 | 10.09 | 1.54 | 0.582 | | | 8.47 | | | 2 691.05 | | | |
| | 2 | 0.085 | 18.06 | 2.66 | 0.760 | | | 8.05 | | | 1 965.33 | | | |
| 1 | 3 | 0.117 | 50.07 | 1.33 | 1.166 | 0.8 | 0.2 | 7.23 | 7.6 | 0.8 | 1 785.67 | 1 829 | 554 | 0.81 |
| | 4 | 0.079 | 53.87 | 0.89 | 0.584 | | | 6.48 | | | 1 295.26 | | | |
| | 5 | 0.104 | 63.71 | 0.94 | 0.754 | | | 7.54 | | | 1 406.60 | | | |
| | 1 | 0.073 | 34.73 | 0.91 | 0.545 | | | 4.39 | | | 855.38 | | | |
| | 2 | 0.058 | 39.02 | 1.25 | 0.597 | | | 4.56 | | | 880.33 | | | |
| 2 | 3 | 0.213 | 34.21 | 1.13 | 1.010 | 0.7 | 0.2 | 4.81 | 4.6 | 0.4 | 775.37 | 816 | 133 | 0.72 |
| | 4 | 0.076 | 38.30 | 0.95 | 0.578 | | | 5.09 | | | 960.51 | | | |
| | 5 | 0.048 | 27.93 | 1.28 | 0.660 | | | 4.01 | | | 610.25 | | | |
| | 1 | 0.051 | 14.78 | 1.39 | 0.376 | | | 3.89 | | | 584.71 | | | |
| | 2 | 0.070 | 25.98 | 1.12 | 0.704 | | | 3.23 | | | 676.30 | | | |
| 3 | 3 | 0.082 | 40.25 | 1.03 | 0.596 | 0.6 | 0.1 | 5.38 | 4.0 | 0.9 | 550.74 | 601 | 46 | 0.71 |
| | 4 | 0.073 | 25.45 | 1.30 | 0.562 | | | 3.06 | | | 598.64 | | | |
| | 5 | 0.092 | 32.30 | 1.12 | 0.705 | | | 4.37 | | | 595.56 | | | |
| | 1 | 0.073 | 34.25 | 1.05 | 0.615 | | | 4.52 | | | 653.21 | | | |
| | 2 | 0.073 | 23.57 | 1.40 | 0.541 | | | 3.72 | | | 723.92 | | | |
| 4 | 3 | 0.079 | 31.19 | 1.49 | 0.520 | 0.6 | 0.1 | 3.86 | 3.2 | 1.2 | 490.41 | 593 | 204 | 0.65 |
| | 4 | 0.089 | 22.17 | 0.71 | 0.656 | | | 2.79 | | | 804.63 | | | |
| | 5 | 0.077 | 12.04 | 0.81 | 0.523 | | | 1.31 | | | 291.73 | | | |
| | 1 | 0.098 | 51.35 | 1.70 | 0.906 | | | 6.22 | | | 1 025.21 | | | |
| | 2 | 0.130 | 20.59 | 1.55 | 0.956 | | | 5.54 | | | 538.54 | | | |
| Function. graded | 3 | 0.142 | 41.76 | 1.20 | 1.050 | 0.9 | 0.1 | 7.26 | 6.0 | 1.5 | 1 176.38 | 870 | 290 | 0.73 |
| | 4 | 0.070 | 15.76 | 1.33 | 0.715 | | | 3.59 | | | 581.59 | | | |
| | 5 | 0.123 | 39.96 | 1.49 | 1.090 | | | 7.18 | | | 1 028.88 | | | |