

# **The Influence of the Molecular Structure of Used Polyolefins on Selected Properties of Foams.**

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Master's thesis  
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**Tomas Bata University in Zlín**  
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**V rámci diplomové práce student:**

- vypracuje literární rešerši na dané téma;
- provede optimalizaci přípravy chemicky lehčených pěn ze směsí polyolefinů;
- provede charakterizaci fyzikálních vlastností připravených pěn;
- bude studovat vliv různého složení směsi LDPE/LLDPE na morfologii připravených pěn s ohledem na velikost a počet pórů.

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## **ABSTRAKT**

V rámci diplomové práce byla vypracována literární rešerše týkající se vzniku porézních struktur, zpracovatelských technologií výroby pěn, materiálů vhodných k jejich přípravě a aplikačních možností napěněných produktů. S ohledem na motivaci připravit pěnovou strukturu požadovaných fyzikálních vlastností při využití materiálů šetrných k životnímu prostředí, byla zhotovena studie zaměřená na vliv molekulové struktury polyolefinů na vybrané vlastnosti navržených pěn, při zajištění snadného procesu výroby a získání vhodných charakteristik určujících požadovanou kvalitu finálních pěn. Součástí této práce je také experimentální část, v rámci které byly připraveny vzorky pěn z nízko-hustotního polyetylenu s rozdílným obsahem lineárního nízko-hustotního polyetylenu o definované molekulové struktuře, přičemž sledované vlastnosti pěn souvisely s jejich aplikací v oblasti tepelné izolace. Dále byla provedena charakterizace výsledných vlastností a morfologie získaných pěnových struktur za pomoci diferenční snímací kalorimetrie a snímací elektronové mikroskopie, dokazujících výhodnost přídavku lineárního nízko-hustotního polyetylenu zajišťujícího strukturu vhodnou pro vznik, růst a stabilizaci pórů. Pozornost byla věnována také významnému faktoru viskoelastického chování polyetylenových pěn, stanovovaného za použití dynamické mechanické analýzy.

**Klíčová slova:** Polyolefiny, Nízko-hustotní polyetylén, Pěna, Porézní struktura, Viskoelastické vlastnosti.

## **ABSTRACT**

The Master's thesis is composed of a literature review describing a formation of a porous structure, processing technologies of the foam production, materials suitable for a foam preparation and application possibilities of the foamed products. This study was focused, with the respect to the main motivation, on the preparation of foam structures with desired physical properties, by using environmental-friendly materials. Therefore, the influence of molecular structure of used polyolefins, on the selected properties of prepared

foams was studied simultaneously with regard to gain proper characteristics determining required quality of final foams. An experimental part was performed in order to prepare foam samples of a low-density polyethylene with addition of linear low-density polyethylene of defined molecular structure in different ratios, whereas the properties have been kept in accordance to application in thermal insulation. Further, investigation of the properties and morphology of prepared foams was carried out by utilization of differential scanning calorimetry and scanning electron microscopy, which have proven profitability of linear low-density polyethylene addition, providing suitable structure for bubble formation, growth and stabilization. An attention was also given to important factor of viscoelastic behaviour of foams, determined by dynamic mechanical analysis.

Keywords: Polyolefins, Low-density polyethylene, Foam, Porous structure, Viscoelastic properties.



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*“There is no such a mysterious and fascinating structure like a Foam is.*

*You can see it while growing on the top of water table, you can hear it murmur when walking along the seaside, and you can taste it while enjoying your morning cup of cappuccino.”*

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I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

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Pavína Plšková

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## INTRODUCTION

A foam is a substance composed of a gas enclosed inside a liquid or solid matter; therefore, foams can be distinguished to solid or liquid. Polymeric foams, as we are using in a daily life, are divided on closed-cell and open-cell foam structures. The difference is in not only a cell structure, but also primarily in foam's characteristics and properties, including mechanical as well as physical and thermal properties and hence main purpose of each foam is determined just by a cellular structure [1].

Study of a cellular structure have a large importance on two interacting segments describing the dependency between a foam morphology and macroscopic properties, chemical composition of matrix and the mechanism of foaming [2], predicate of such material possessing relatively low density is suitable for an acoustic and thermal insulation [3].

Several additives having a various effect on final structure are available on the market. Among the most often used additives for foaming belong blowing agents, cross-linkers and catalysts affecting not only mechanical properties like strength but also for example physical properties like density.

A foam developments and novelties from the field of foams, progress forward more and more every day, because of its popularity and different properties unlike any other material, providing a wide range of its usability. Hand in a hand with a progress, branch of foams impinges on such a different challenges and rising requirements including improved non-flammability, non-toxicity and low environmental impact [4].

Many studies were carried out [5, 6] on the topic of polymeric foam's morphology. Rodriguez-Perez et al. [7] have measured the evolution of the gas pressure in the closed-cell low density polyolefin foams as a function of time, and it was obtained that amount of gas pressure significantly affects the mechanical and thermal behavior of low density flexible polyolefin foams.

Polyolefins (*PO*) used in this study, namely low-density polyethylene (*LDPE*) and linear low-density polyethylene (*LLDPE*) were blended with a blowing agent (*BA*) and crosslinking agent to obtain desired properties.

Rodriguez-Perez have also studied [8] a dynamic mechanical analysis of several foams including LDPE+LLDPE blends with regard to their applications, and he found the relation between applied frequency and final properties of foams [9].

The mechanical response of foamed plastics is important for choosing the suitable material for each application therefore, in this study dynamic mechanical analysis (*DMA*) was performed to determine viscoelastic behavior of prepared foams. Differential scanning calorimetry (*DSC*) and Scanning electron microscopy (*SEM*) were successfully employed for a characterization of morphology of foamed sheets. Determination of insulation properties were based on thermal conductivity measurements carried out by using a thermal conductivity analyzer, in order to describe a main applicability of prepared foams. Bearing this, interdependency of morphological parameters, molecular structure and final properties (dynamic mechanical behavior in compression, apparent degree of crystallinity, cell size and size distribution) were defined in this study.

## **I. THEORY**

# 1 CHARACTERIZATION OF FOAMS

Polymer foams became as two-phase materials into one of the most used products in a modern life, with importance in building and construction segment, furniture, packaging, automotive and transportation, and increasingly also as shoes, accessories for a leisure time and sports materials [2]. It is given by unique properties of polymer foams such as its lightweight and buoyancy, which provide many advantages with reasonable economic, environmental or technical aspects [10]. The main advantage comes from the ability of energy absorption (vibrations and sound) resulting in one of the most interesting final application [2]. It is no wonder, that the production and usage of polymers and polymeric foams, enhance obviously human's life standards.

Cellular plastics (as plastic foams are often called), known for their dielectric properties, play a key role in insulation applications due to the gas, or free space, respectively entrapped inside the continuous polymer matrix. As was already mentioned in the introduction, open or closed-cell structures are described as two different morphologies affecting diversity of final foam's properties such as flexibility or rigidity, insulation abilities and density [5].

Nowadays the consumption of polymer foams still raises because of its fast and cheap production and the most often used polymers are kept in a sequential row: polyurethane (*PU*), polystyrene (*PS*), polyvinylchloride (*PVC*) and polyolefins. All types of polymers meet the requirements to be foamed as far as the gas is generated within a polymer foaming process [2]. Change (reduction) of density of polymeric material is then the result of foaming process, while a wide range of densities can be produced [2].

Cellular structure almost identical to polymeric foams or sponge plastics are favourably employed not only as products prepared synthetically, but also by nature itself. One reason might be the fact of excellent constructional properties of a solid foam structure therefore we can find it in the structure of woods, plant *parenchyma* [11] or a human trabecular bone [12, 13]. Cellular structure conformable to the one of examined foams have also porous minerals and beeswax honeycomb. Scanning electron microscopy imaging of a cork looks very similar to the image of closed-cell foam structure [13]. Bio-mimicry is a modern trend



and design solution with inspiration from nature used in furniture designing [11]. Conveniently, solution should pay attention on nowadays environmental and ecological issues; therefore, sustainable sources are frequently sought, to produce eco-friendly plastic foams for instance these frothed by a less harmful carbon dioxide [14]. Zach et.al have investigated thermal insulation properties of natural based foams prepared from a hemp fibers [15]. However, there are more interesting and not too familiar examples such as froth cover made by spittlebug nymphs to protect themselves before predatory ants by engulfing themselves inside the foam shield containing ant-repellent chemicals to hide from danger and keep in safe [16].

Arencón et al. [6] have tested several polyolefin-based flexible foams in order to study its cellular morphology or fracture behaviour. Foam extrusion was used to produce polyethylene and polypropylene foams. Essential work of fracture (*EWF*) took a place to evaluate an effect of foams chemical nature or expansion ratio on the fracture parameters.

## 1.1 History

Foams and its lightweight properties were already used advantageously within Second World War (*WWII*), and from that time, the foam evolution made a huge step forward. Thus new developments in foams and foaming chemistry, have followed a polymer boom in 1930 because of useful behavior, and has started progress in polymer industry including research of new materials or developing new technologies. Some of the properties including insulation and cushioning are very interesting from the application point of view similarly as their low density allowing a flotation on a water surface [17].

First, there were only few polymer materials such as polystyrene (*PS*), nylon (*PA 66*) and polyurethane (*PU*). The polymer foams development has started with a science by research around 1930–1950 followed by improving technologies in 1950–1970 and continue up today with modern innovations on the field of final applications [17]. As a first thermoplastic foam is considered extruded polystyrene arranged by *Dow* during a *WWII*, which was reported by Okolieocha et al in their paper [18]. Extruded *PS* was thus well-known and widely used material in that time, next to *PU* which it was easy to foam even with no addition of a blowing agent, simply foamed by polycondensation process.

Moreover, in 1980s the polymer foam industry became a solid reality after applying in wide range of other industries, for instance automotive, medical, military and recreation [17].

The first mention about polyethylene foam is dated in 1960 and belongs to Rubens et al, scientific group from *Dow Chemical*, who found out a cross-linked polyethylene (X-PE) having a suitable strength to be foamed [17]. The innovation trend of foam technologies and foam science is successively continuing through modern applications in next century.

Daily topics of recycling possibilities, healthcare and environmental aspects have resulted from everyday novelties and necessities or rather threats in the region of polymer foams. Another issue concerning a diminution of raw sources, which are essential for polymer production and absence of landfills where a waste of non-recyclable materials can be stored. On the other hand, a cheap plastic production comes from countries out of Europe, where the regulations are much less strict than in European Union.

## **1.2 Application**

In general, progress within expanded plastics meets a development traces in following steps: as first, there is an idea requirement clarified by a science, then a proper technology need to be developed and applied to capture desired properties, which must be regulated later. Innovation is an important aspect of accelerating growth of different options and possibilities within the field of flexible, semi-flexible and rigid foams offered by various additives such as pigments, flame-retardants, blowing and nucleating agents.

Nowadays world of polymers arranges variety of different and unique material properties thanks to a possibly different crystallization and melting behavior of every single polymer conferred by its molecular structure, which is defined by chemical covalent bonds and van der Waals inter-bond forces. It means there is a wide range of applications depending on desired properties of a final product [19].

Several simple ways of changing even mechanical or physical properties of processed foams by varying procedure methods are available and thus allow choosing numerous polymers of different material characteristics. Therefore, when compare to

conventional materials, it is quite easy to design and prepare wanted polymer product with specific properties suitable for every each final application [20].

The primary aim to fabricate the foam plastics, is not only material density reduction and thus significant reduction of the material consumption without considerably affected of their crucial properties, finally lead to the overall cost reduction [18]. Plastic foams are easily produced with comfortable application for many purposes (thermal and acoustic insulation properties) already described above [21]. Furthermore, polyolefins benefit among other polymers (PU foams) is recyclability, chemical resistance and inertness [22] and they are considered as a non-toxic in a fire [9]. To the most preferred applications with respect to light weight and buoyancy as well as compressibility can be mentioned aviation [23], construction cushioning, damping systems [22], seating, mattresses [24], core of sandwich panels, packaging [22], electronics devices packaging [25], recreation, furniture [5], flotation and sound attenuating [26] as favorite parts of floor underlay in gyms or warehouses [17]. Several applications cover a variety of industries including marine, medicine, automotive or transport and sports and leisure market [24].

Another specialized matter of interest is involved in tissue engineering, which finds new opportunities of cellular structure in providing synthetic porous scaffold, which substitutes the body's extracellular matrix, when occurs damaged or diseased tissue. The example of suitable material can be taken a poly-L-lactic acid (*PLLA*) suitable for skin, nerve, cartilage or internal organs [27].

## 2 MATERIALS USED FOR FOAM PREPARATION

To understand the definition of a foam, there are solid and liquid foams. Solid foam can be classified as a material where the gas is dispersed in a solid substance while liquid foam is dispersion of a gas bubbles in liquid substance [28].

Sufficient flexibility and strength of a material are important parameters to define a foamable structure able to hold an expansion, which takes place within a frothing at elevated temperature. Temperature and shear history thus play a substantial role in extrusion foaming because of heat distribution, which might, when not sufficient, negatively affects qualities and homogeneity of product, but also might lower the strength of material which, as already discussed, is very important to be kept in a high level for fluent bubble formation. In other words, the increase of a foaming temperature requires a higher material strength [17].

Different materials and their characteristic temperatures affect a structure of final foam, depending on glass transition temperature ( $T_g$ ) of used polymers (whether lies below or above the room temperature), so that foams are distinguished as flexible or rigid [4]. However, the resulting flexible or rigid polymer foam structure depends simply on a chemical nature of used polymer matrix, whether the matrix was subjected to cross-linking and depends on a presence of hydrogen bonds between molecules. On the other hand the resulting cellular structure in the term of cell shape, size and distribution is influenced by a process conditions and chosen foaming technology [29].

Among typical foaming polymers belong polyethylene glycol terephthalate (*PET*) often used in a food-packaging segment. Another long-time favorite polymeric material suitable for foaming preparation is polyurethane. If polycondensation is carried out within a polymerization reaction, a gaseous byproduct may be generated spontaneously and acts as a blowing agent, for instance in the cases of di-functional substances like a PU foam.

Another essential polymer is widely used polystyrene, which is in a form of foam used mainly as a building insulation. PS have generally foregone the foams prepared from polyolefins, primarily due to a material properties such as  $T_g$  typically near to 100°C providing to PS good strength and rigidity while using at room temperature [2]. It is

noteworthy that even though polyethylene (*PE*) is not amorphous as *PS*, and exhibits a different  $T_g$ , it can be foamed after adequate cross-linking.

## 2.1 Metallic Foams

Liquid or powdered state of metals can be used to produce a solid foam by either direct or indirect method. Liquid metals are usually foamed directly by using gas-releasing agents or by injecting a gas. Straightly injected gas into the molten metal should be preserved from fast bubble escape onto the surface of high-density matrix, by increasing a melt viscosity [12]. Gas injection is commonly used in the process of foaming due to a large productive volume and continuous production. Indirect method of metallic melt foaming is performed by casting around a solid filler or by a method called investment casting as can be seen in the Figure (1). During investment casting a molten metal is cast into prearranged gaps having an inverse shape of final foam. Polymeric foam binder is full-filled with a high thermal resistance material while proper drying a polymer skeleton is removed and generated empty voids are filled by a metallic melt [12].

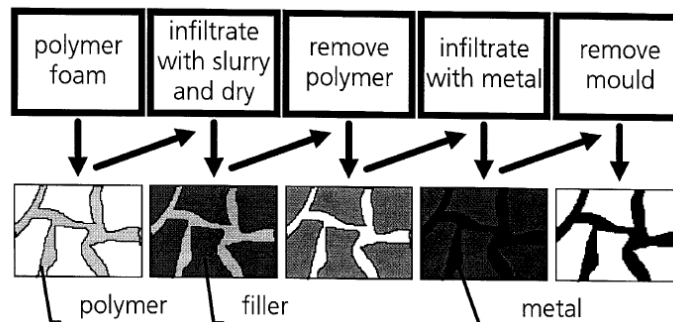


Figure (1): Investment casting method of metallic foam production[28].

When processing powdered metals, the porous metallic structure can be obtained by sintering a powder or fibers. Within a sintering treatment, as shown in the Figure (2) [28], adjoining particles sinter and stick together while forming an interfacial area. Metals like titanium or stainless steel are widely processed using this method[28][28].

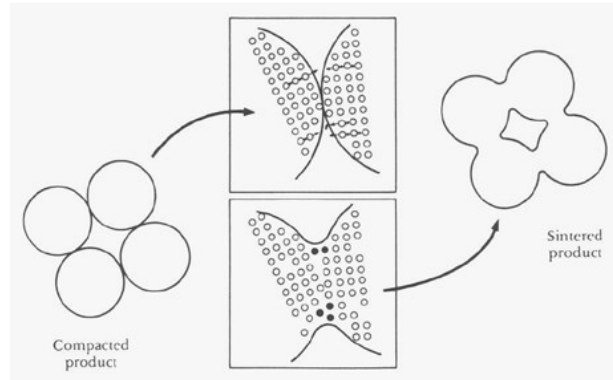


Figure (2) Procedure of metal powder sintering.  
*Up: compacted product; down: sintered product.*

Other methods and processing techniques of metallic foam production are well known and commonly used, for example a vapor deposition or electrochemical ions deposition [30].

Reasons for foaming the metals are very similar to these for a polymer foaming, meaning the aim of combining contrary properties in order to form product with a profitable performance [31]. Hence high stiffness and low specific weight is often an advantageous combination for various applications such as constructions, but there are more possibilities like damping or filtration purposes [12]. Among general properties of metallic foams belong excellent absorbing properties with importance at absorption of energy, sound and energy from vibrations. Moreover, beside polymeric foams they have good magnetic shielding properties [32]. Functional and structure applications include automotive industry, where metallic foams for instance in a form of sandwich panels, reduce a weight of vehicle and thus lower a fuel consumption. The same function means advantage also in aerospace industry and shipbuilding. Solid foams stay forefront in a crash energy absorption and can be useful as flame arresters. Foamed metals perform no less important function in biomedical applications, where a magnesium can be used as bio-degradable implants serving as a load-bearing structure for a growing bone not only at the stage of convalescence [28]. Titanium foams can acts as a scaffold in trabecular bones in tissue engineering [13].

## 2.2 Polymeric Foams

### 2.2.1 Cellular Rubber

Cellular rubber is known also as a foam rubber, and is the air-filled material commonly used as an acoustic absorber made of natural rubber or latex [33]. Solid rubbers may transform into elastomeric foams by adding vulcanizing and blowing agents. The bubble formation is initialized due to the presence of micro voids inside the elastomer. General aspects of a rubber foaming are given by temperature dependence of viscosity and a relationship between viscosity and the decomposition temperature ( $T_d$ ) of the blowing agent. Initial heating reduces a viscosity of the system until the vulcanization temperature is reached, conversely at this moment, vulcanization begins and viscosity increases. Whether the open or closed cell will generate, depends on elected blowing agent and its temperature of decomposition. Open cells are formed by using a blowing agent with  $T_d$  lower than the minimum reached viscosity. This is because of sudden expansion followed by wall thinning and consecutive rupture, which might occur before its stabilization with cross-linkers. On the other hand, if there is used a blowing agent with  $T_d$  closer to increase of viscosity, closed-cells are created since the bubble walls are cured and thus strength enough [6].

### 2.2.2 Polyurethane Foams

PU foams are favorably used in a wide range of applications due to its simple preparation and variability in many purposes. The most world wide-known application are bed mattresses and for example soft and flexible part of car seats [34].

Altering a ratio of used reactants or change in degree of polymerization results in differences in structure of final foams in the term of obtaining a soft or rigid form. Foaming proceeds in the time when two reactants are merged in a mixing chamber and carries on while polymerization reaction begins. This simple and direct way of PU foaming allows to use different methods of foam preparation with respect to requirements on a final product. There is a *foam-in-place* method, which provides to fill empty place with a product, or to produce a multi component part by direct foaming in exact place. Another method is a

*foaming-in-mold*, using injection molding or reactive injection molding, to achieve demanded shape and size of product, corresponding to the shape and size of used mold. This way include open place foaming (for instance on conveyer belt) in order to obtain foamed semi-product reliant on further post-processing operations. Alternatively, there is *spray-in-place* method, where the mixture of two reactants leaves a mixing chamber through a spray nozzle, sticks on a wall and foams in a vertical position, which provides easy way of applicability of foams in building and construction segment [17].

### **2.2.3 Thermoplastic Foams**

Thermoplastic materials like polyolefins have less rigidity of polymer chain which is preferable for foaming process because of elastic behavior of branched polymers, which is important for radial expansion, having an effect on foam extrusion process [17].

As it was proven before, that inert solid particles act inside the material to be foamed, as nucleating agents, which generate higher amount of small pores than is obtained while self-nucleation process. Therefore, higher effectivity of bubble formation and thus better cell size distribution is observed, while foaming polyethylene supersaturated by gas or volatile compounds. As effective nucleating agent can be used some of components of a group of reactive materials, which decompose exothermally and therefore form localized hot spots, which work as proper place for bubble growth initialization. Azodicarbonamide (ACA) exhibits a great importance in the role of dynamic nucleator, which forms hot spots. As another nucleating agent is considered a metal powder, which after swelling and cooling the polymer within foam extrusion, remains hotter than the polymer and acts as hot spots itself [6].

#### **2.2.3.1 Polyolefin Foams**

In general, PO are noted for properties such as chemical and abrasion resistance or toughness and flexibility. To compare them with a flexible PU foams, still PO semi-rigid foams are considered as the firmer one. Most of the obtained cellular structures are defined as closed-celled, which provides several applications of PO foams [35].



Polyethylene was chosen in this study because of several reasons and belong to the group of commodity materials with fast and cheap production, PE is recyclable [36] and has a  $T_g = -120\text{ }^\circ\text{C}$  and  $T_m = 115\text{ }^\circ\text{C}$  [19].

Crystallinity of polyethylene depends on a cooling rate. LDPE due to a long side branches crystallize to app. 40-50% and this is confirmed by reciprocal influence of the degree of crystallinity, density and its overall strength [19].

Cross-linked polyethylene foams are favorably used due to their facility for thermos-fabrication and thanks to their desirable properties such as resiliency and small size of closed cell construction [37].

One of the most common technology to process PO foams is an expansion process, which runs in a molten state of polymer matrix while spreading a gaseous phase throughout the melt. Expansion process comprises basic sections such as bubble initiation, bubble growth and stabilization, as will be described following in a chapter 3 [35].

The common utilization of LDPE foams is due to their good properties possible to advantageously combine, like sufficient mechanical strength, good processability, high resistance to chemicals and low cost in comparison to other materials [21].

### 3 FOAM FORMATION

Undisturbed preparation of polymeric foams includes some features providing continuity of the foaming process, such enough soluble gas, bubble nucleation and growth or phase separation, and lastly stabilization of final product, whereas foam formation and its bubble nucleation is driven by thermodynamic rules [17].

Foaming of cross-linked materials was developed thanks to the increase of material strength by setting new chemical bonds, which is with advantage used especially for polyolefins like polyethylene. Cross-linking agent is simply blended with a blowing agent, polymer matrix, and forms a homogeneous melt [17].

The importance of a melt viscosity in a foaming process is shown in Figure (3) [4]. Nucleation starts in a low viscosity melt. Bubbles can growth thanks to a raising viscosity and increasing melt strength able to persist pressure increase within expansion. Last step is described as a stabilization, when the viscosity is high enough to avoid a bubble collapse or rupture.

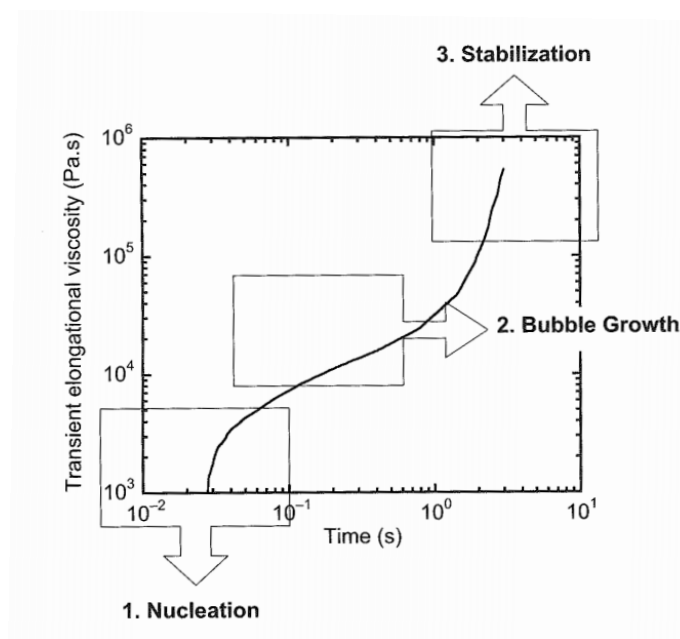


Figure (3): Bubble nucleation, growth and stabilization in dependence on elongational viscosity

As a driving force of foam formation is considered a sudden reduction of gas solubility released by blowing agent dissolved in polymer. This abrupt change may be caused by change of external conditions such as pressure, temperature or stress [4].

As a simple way of foam formation one can consider mechanical or physical method. Mechanical way is based on whipping of gases into a polymer melt or solution while physical way of bubble formation is represented by volatilization of low-temperature boiling liquids or by gas dissolved in a polymer matrix, which expands after pressure reduction [10].

There are several methods how to prepare required foam structure including compression moulding, reaction injection moulding or the most often used injection moulding of expandable beads and extrusion process. Extrusion foaming includes a foaming of cross-linked material by tempering and activation of blowing agent or decomposition of a chemical blowing agent at elevated temperature. Final form of produced product depends on complexity of selected method. Other techniques as lamination of foams or foam composites production present processes that might be even more complicated [10]. When blowing agent is added, pressure reduction at elevated temperature between  $T_g$  and  $T_m$  then causes foaming of treated material [17]. Thermoplastic foams are generally formed by blending with foaming agent, which after melting dissolves and distributes throughout the molten matrix and cooling down to stabilize, when the bubble growth by gas expansion is finished [6].

To compare injection to extrusion foaming process, the extrusion foaming is a continuous process with fast production speed while injection moulding periodically requires systematically injection of molten material, extraction and repetition. Modern methods, however, improving multi-moulds machines resulting in comparable productivity as extrusion moulding and beyond everything there is a material save, profitable by usage of expensive polymers [17].

As mentioned above, there are mechanical, chemical or physical ways of foam formation providing different methods and various possibilities how to prepare preferred

cellular structure with desired properties of final foam [10]. Three general principles how to put the gas inside creating bubbles are [6]:

- Simple air whipping to the fluid represents a mechanical method;
- Dissolution of carbon dioxide in the liquid under the pressure or usage of low-boiling liquids, which gives a gas after heating belong to physical method;
- chemical method meaning chemical or polymerization reaction proceed like isocyanate and water; or chemical decomposition of blowing agent.

### 3.1 Bubble Nucleation

Diffusivity of a gas generated within foaming process, affects nucleation and bubble growth. High diffusivity helps to make nucleation faster and thus create a finer cell structure [4].

Initiation of bubble formation can start purely as a self–nucleation, when the bubbles start forming inside a homogenous matter with no presence of any other substances, neither particles nor gases. As a second option there is a heterogeneous system comprised of two phases, where the phase presented in polymer matrix makes a proper environment for bubble formation. Therefore, bubbles are formed much easier at the interface between solid and liquid phase and the solid particles acts as nucleating agents. Instead of solid particles there can be presented micro-bubbles, causing a bubble growth. Essential condition of bubble formation is an increase of free energy of the system to be foamed [6].

$$\Delta F = \gamma \cdot A \quad (1)$$

Where  $\Delta F$ ,  $\gamma$ , and  $A$ , respectively has a meaning of free energy of the system, surface tension of the liquid, and total interfacial area, respectively. Decrease of a surface tension by emulsifiers or wetting agents, decreases the value of free energy that is needed for start of bubble formation as defined in equation (1). Presented equation (1) explains the fact that for a given volume of the foam is more stable that one with fewer number of larger cells [6].

The beginning of bubble formation process subjects to conditions of thermodynamic equilibrium. For starting a foaming procedure, only the exact amount of

gas molecules are needed to be intercalated within the polymer matrix. Since the polymer chains does not tightly align on each other, there is enough free space inside or free specific volume, respectively, to catch the gas bubbles. However to gain a beginning of a bubble nucleation and a growth the polymer system should meet the condition of “critical bubble radius” which is defined as

$$R_{cr} = \frac{2 \cdot \sigma}{(P_b - P)} \quad (2)$$

Where  $\sigma$ ,  $P_b$ , and  $P$  represent surface tension, bubble pressure, and surrounding pressure, respectively. The critical bubble radius ( $R_{cr}$ ) is thus an overlapped threshold reached by clustering enough gas molecules [17].

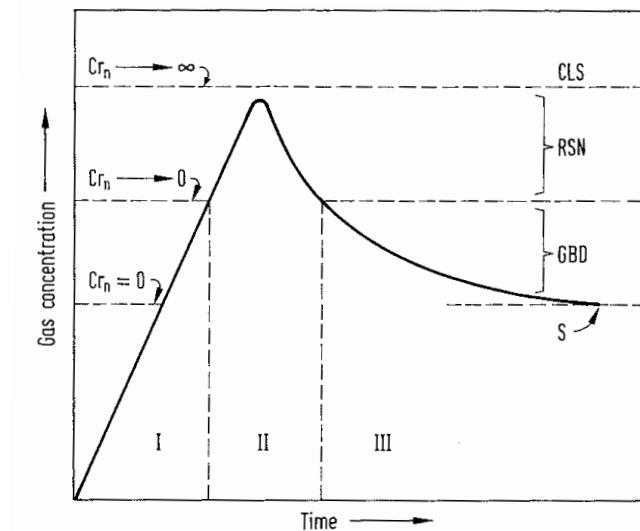


Figure (4) Relation of gas concentration changes and nucleation and growth of foam cells, where  $Cr_n$  = Nucleation rate;  $CLS$  = Critical limiting supersaturation;  $RSN$  = Rapid Self-Nucleation;  $GBD$  = Growth by Diffusion;  $S$  = Saturation [4]

Figure (4) describes a relationship between gas concentration and nucleation and bubble growth, respectively. A liquid system containing a foaming gas with no presence of nucleating agents nor micro-voids inside is assumed. First region (I) refers to solution saturation. Gas concentration raises until the saturation equilibrium is reached and then with higher gas income, a self-nucleation begins. During a region (II) the gas concentration

remains at its critical value and self-nucleation continues. When enough bubbles are formed and the gas concentration decreases under the critical point, no more bubbles generate; however, the diffusing gas causes a bubble growth in region (III). After reaching a saturation level of gas concentration (S) also bubble growth stops immediately.

### 3.2 Bubble Growth

Already initiated bubbles will grow inside the molten polymer by process called coalescence, which means coupling of two or more bordering bubbles. This can be caused due to an expansion of bubbles by increase of heat or due to a gas diffusion into the bubbles. The latter one is confirmed by an equation (3), where the smaller radius means higher pressure inside the bubble within an equilibrium and the gas pressure is larger in a spherical bubble than the pressure in surrounding fluid. This also follows a theory of equation (4), where the pressure difference, which is given by different bubbles radii, leads to the gas diffusion from a smaller to the larger bubble [6].

$$\Delta p = \frac{2 \cdot \gamma}{r} \quad (3)$$

$$\Delta p_1^2 = 2 \cdot \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \quad (4)$$

Both mentioned factors result in the assumption that during a sufficiently long time, the growth of larger sized bubbles is preferred over the smaller pores hence the fine bubbles disappear [6].

A shape of growing bubbles differs during each individual stage of bubble growth. In the beginning, only small volume of gas is present in a polymer matrix and bubbles grow in a spherical shape. After the gas volume increases but surrounding phase ceases to sustain in a spherical shape, then bubbles start to change its shape on polyhedral. Dwindling phase of polymer melt forms boundaries and corners between two or three adjacent bubbles. In low-density foams production there are dodecahedron-shaped bubbles with four- and five-sided thin borders, made of solid phase membranes [6].

Adequate amount of blowing agent is necessary to add in a polymer matrix to gain an efficient cell growth, which is dependent on a gas pressure produced inside the cells, and depending on solubility and diffusivity of a blowing agent in polymer [4]. Bubble growth runs continuously until the rupture occurs or the bubble is stabilized [35].

### 3.3 Bubble Stability

As it was described in the chapter of foam formation, it is necessary to stabilize foamed polymer because of its thermodynamic instability, surface tension and gravity, which all can lead to a foam collapse. To capture a stable foam, there should be adsorbed an emulsifier at the surface of a liquid phase of foam. Therefore, one can control the surface tension by varying the type and concentration of the component adsorbed on the surface, which is also described by a Gibbs theorem:

$$d\gamma = -\Sigma\Gamma d\mu \quad (5)$$

Where  $\Gamma$  stands a surface excess of the adsorbed component and  $\mu$  its chemical potential. The equation (5) represents a dependence of the surface tension on concentration of adsorbed solute. A detailed principle is, that when only limited amount of the adsorbed component is available, then increase of the surface area leads to decrease of  $\Gamma$ , therefore raises  $\gamma$ , and so the resulting effect works against the surface extension. In other words, wall thinning is suspended and the process acts as a stabilizing factor [6].

Theory generally describes two processes providing a recovery of concentration of surface adsorbent, which is reduced during a bubble expansion. There is the Marangoni effect and the Gibbs effect working on two different principles. The first named Marangoni effect has a self-healing attribute and causes a flow of the surface layer from the areas of low surface tension to the areas of a high surface tension (with a low concentration). Thus, the membrane thickness is restored due to a layer flow and membrane elasticity is maintained. On the other site, there is a Gibbs effect, which refills the concentration of the surfactant by its diffusion from interior of the liquid to the surface [6].

A foaming temperature, as a second parameter affecting foam stability influences a viscosity and surface tension thus supports the membrane thinning and so a rupture of the

wall, may occur. Van der Waal's forces attracting each other among the surfaces of very thin adjacent walls can cause even further thinning [6].

Other stabilization effects provided by additional forces are important rather in the initial stages of bubble growth until the foam is in a liquid state. At least a small amount of activation energy is needed during a rupture initialization. Another important stabilizing effect comes subsequently when a viscosity of the foam increases and thus helps to stabilize the foam structure [6].

Stabilization of formed bubbles can be carried out by physical or chemical way. Physical stabilization proceeds when PBA is used during a polymer foaming. Stabilization process works on a principle of strain hardening of cell walls because of biaxial stretching while a rapid increase of elastic modulus of polymer matrix occurs. Additionally a rapid strain rate due to a diffusion of blowing agent helps to improve the strain hardening. Another case is described for a chemical foaming in the presence of CBA. Cross-linkers are employed to achieve a sufficient melt-strength, in other words the extensional viscosity of polymer melt is enhanced [35]. More probably, the wall of rigid foam can rupture in comparison with elastic polymeric foams [20]

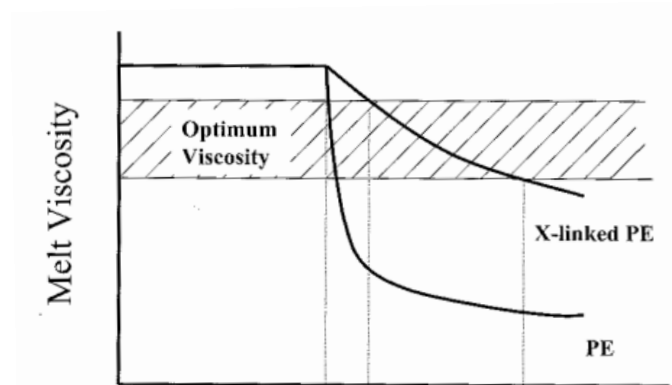


Figure (5): Chemical stabilization by crosslinking.

Influence of cross-linking effect is shown in the Figure (5) [35]. As a result is extended plateau of optimal viscosity of X-PE, in which polymer melt has a rubbery state hence elongation viscosity of polymer melt increases. Therefore, range of proper processing temperature is broadened. In addition, cross-linked PE have an advantageous properties like a good stability against ultraviolet radiation and weathering [38].





## 4 CELLULAR STRUCTURE

Cellular structure and porous materials are often applied with a favor in different segments thanks to its variability in properties. Valuable advantage of cellular is that only a small amount of polymeric material is needed to gain a quite rigid and strength structure, what means in many cases an economic benefit [17].

With material expansion caused by a foaming process, goes hand in a hand modification of volume, obviously. Once the same amount of matrix material occupies in a very short time larger space, density as a material characteristic transform significantly [17]. Density of polymer foam is defined as:

$$\rho_F = \frac{W_p + W_g}{V_p + V_g} \quad (6)$$

where  $\rho$ ,  $W$  and  $V$  signify density, weight and volume while subscripts  $F$ ,  $p$ , and  $g$  means foam, polymer, and gas, respectively. In other words, it means the more gas is trapped in the foam structure, the lower density of foam will be obtained, because of a high weight to volume ratio of gasses [17].

Porosity, in general, characterizes the porous materials and works as a statistical parameter for studies of gas-filled systems. However, foamed polymers differ in comparison to inorganic porous materials in the terms of interactions between polymer matrix and foaming gas phase. It means that chemical nature of the gas produced by blowing agent affects the behavior and physical properties of the foamed polymers [2].

Cellular structure reproducibility is usually provided by a heterogeneous nucleation which is thus preferred in order to perform better control of nucleation process [4].

### 4.1 Porous and cellular systems

Cellular structure as a two-phase system can be characterized by quantitative parameters described in the Figure (6), which differ from each other depending on describing phase. There are typical characteristics of polymer phase and gaseous phase [20].

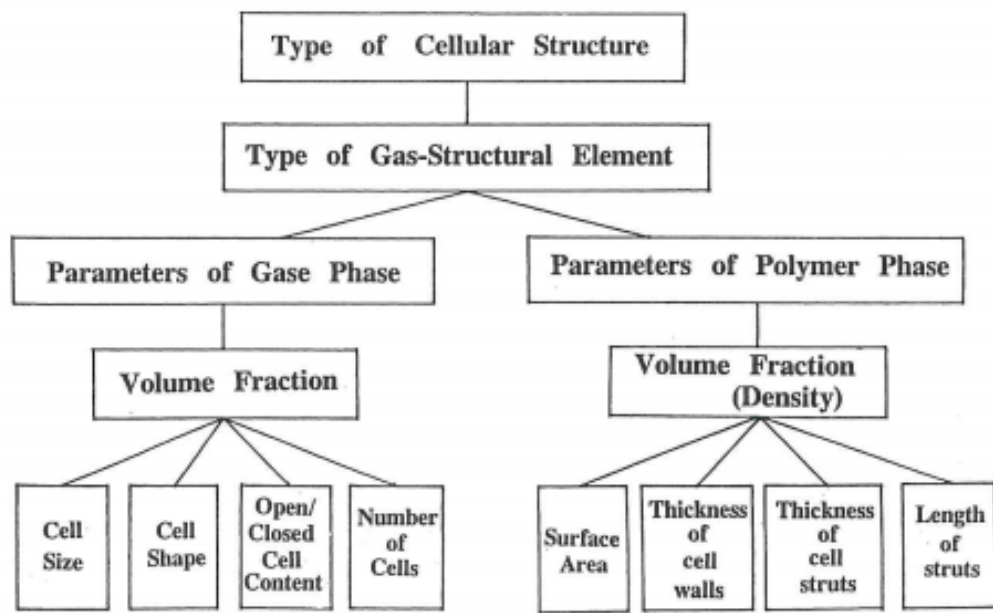


Figure (6): Typical parameters of cellular structure characterization.

The main properties and parameters characterizing porous and cellular systems have been describing for a long time by foam morphology including a description of internal structural elements (pores and cells) and their size and shape. Recent developments however have revealed a fact about the influence of intercellular space on final properties of foamed products. Due to a foam density, it was roughly assumed that gas-filled polymers behave with respect to the gas phase and accompanying number of pores, their morphology and a degree of closeness. Nowadays it tends to opinion that size, shape and thickness of walls or ribs of cells influence basic properties such as elasticity and strength of foam [2]. Wall thickness also dramatically influence a foam weight, logically [17].

## 4.2 Open and Closed Cell Structures

Closed-cell foams contain closed bubbles, surrounded by a matrix material and differ in a wall thickness and thus overall strength, while for open-cell foams are typical junctions between bubbles with incomplete boundaries [20], so adjacent bubbles are tunneled [6] as pictured in the Figure (7) [18].

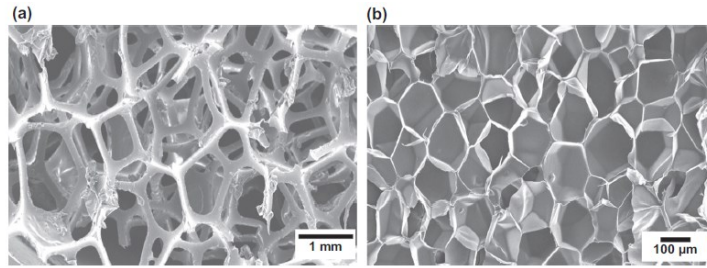


Figure (7) (a) open-cell, (b) closed-cell cellular structure of polymeric foam.

Basic macro structural parameters such as relative number of open or closed cells, a specific surface area, the apparent density and the cell size and shape, have an impact on properties of foamed plastics. Different structure is controlled by various foaming conditions and chemical composition of polymer phase [2].

Open cell structure is engaged by air whereas a hydrogen or carbon dioxide fills the closed cells depending on volatile liquid used within a blowing process. It is assumed that internal gas diffuses out of the foamed material meanwhile the atmospheric pressure penetrates inside [7]. The walls of closed cell gas structural elements thus can burst, or the foam structure might shrinkage, respectively, while diffusion process takes place in a foamed polymer. It happens because of higher diffusion rate of internal gas than the counter diffusion of atmospheric air [2].

Gas-filled polymers contain both isolated and communicating pores (gas structural elements), but generally, only the one structure dominate over another. Hence, it results in varietal purpose of applicability of open and closed cell foams. Foams with a predominantly open cell structures are useful in absorbing and damping sounds, water and moisture absorption. Open-celled have higher permeability to gas and vapor but lower insulation ability unlike the closed cell foams [2].

Open or closed-cell structure, as shown in the Figure (8) [20] is prepared with respect to the purpose of final application properties. While some foam applications require all pores closed, or open, respectively (like for insulation properties) other application need a certain open/closed cells ratio for precise controlling the dynamic of the recovery after compression (for example sealing joints in buildings or roads) [4].

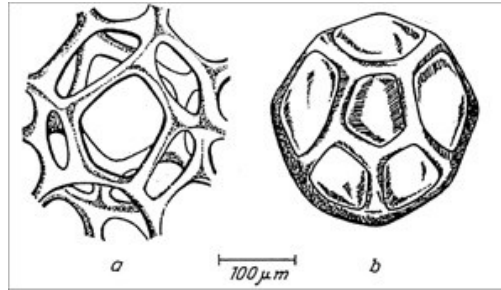


Figure (8): Schematic views of a) open, b) closed gas structural element of rigid foam.

Once the bubble grows in a perceptible size, limit of stressed material is exceeded and a thickness of bubble wall rapidly diminishes until the rupture occurs. This results in open cell structure of foam [17]. When open-cell structure is obtained, there are tunnels between generated bubbles. One should be aware of closed-celled foam tends to volume shrinkage because of pressure differential developing a partial vacuum inside the cell while the wall is not strong enough to withstand the pressure excess [6].

Due to a variation in blowing processes, also formation of open or closed cell structure can be different. However, elastic polymers form open cells in general, while rigid polymers are thought as closed-cell creating materials. Therefore, it can be expected that open-cell structure are formed using phenolic and carbamid foamed plastics. On the other side closed-cells are produced by foaming polyurethanes, silicones, epoxy resins, polystyrene or polyvinyl chloride [2].

A special reticulated structure of foamed plastics can occur when closed-cell foam is produced within a primary blowing and then isolated structural elements rupture in the thinnest point of cell wall during secondary processing methods such as hydrolysis, oxidation, heat, elevated or reduced pressure and mechanical treatment. The resulting reticulated structure as can be seen in the Figure (8) is composed of cells formed from ribs and completely devoid of the cellular walls. Applications of reticulated foams like air filters in engine exhaust systems or damping materials, correspond to their very low densities altering in the range of 3 to 10 kg/m<sup>3</sup> [2].

### **4.3 Cell Shape of Foamed Polymers**

Characterization of cell shape is diversified on qualitative or quantitative methods. The basic understandings lie on assumption of geometric models. However, the real foam is usually more heterogeneous and contains different non-uniform shapes of cells. Among the essential shapes are counted sphere, ellipse, hexagon or polygon while some more various shapes are described as dodecahedrons with pentagonal faces. To cover all described shapes there are widely available complex shape models such as open- or drain-dodecahedrons as well as 14- or 12-faced polyhedrons [20].

#### **4.3.1 Anisotropy of cell shape**

The main difference between theoretically predicted and real morphology structure of foamed polymer is that the real one undergo a shape deformation or elongation in the direction of foaming. Stretching reaches different degrees depending on a foaming, whether the process proceed in a closed space or as a free-rise. Foaming in the mold is considered as a closed space, causes a lower elongation of generating cells, which occurs mainly near the surface layers. Larger stretching and cell elongation is observed along the foaming direction [20].

It should be assumed, that the properties of foams are different along the direction and perpendicular to the direction of foaming, and of course higher performance is achieved along the direction. Mechanical strength, dielectric and thermo-physical properties are therefore affected [20].

### **4.4 Cell Size of Foamed Polymer**

Gas or physical blowing agent, respectively, has a meaningful impact on a cell density. The higher the gas solubility the bigger amount of nucleation centers after phasing out the blowing agent, where the cell growth can continue. Cell density, which depends on nucleation rate, affects cell structure, which thus increases with an increasing amount of a gas. Small-molecular blowing agents such as CO<sub>2</sub>, generate a high cell density structure since the small molecules can easily escape the foamed structure compared to larger molecules such as hydrocarbons which produce low cell density foams [4].

Approximate knowledge of obtained cell size is essential characteristic for designers of manufacturing processes as well as for researchers. It is logical, that the real foam structure consist of not few cells of each different shape, size and volume. There are two options how to qualify the basic characteristics and cell parameters describing its size. The direct method of macroscopic measurements or indirect method of observation such as adsorption or pycnometric and volumetric methods [20].

#### 4.4.1 Cell size and distribution

Cell size and number of cells as one of physical aspects affecting some of characteristic properties of foams. Generally, the cell size and its distribution has an impact on internal surface area which thus has another effect on a sound attenuation which is taken into account for sound isolating applications [17].

Cell sizes and their distribution in the foam are affected by polymer grade but also by a process of foaming and processing conditions. By varying a foaming technology there can be prepared and distinguished fine-celled foams with the cell size between 10  $\mu\text{m}$  – 100  $\mu\text{m}$ ; and microcellular foams of cell size  $\leq 10 \mu\text{m}$  [18].

Parameter characterizing macro-structural homogeneity is described as a number of cells per unit volume of foam ( $N_c$ ) and is frequently used to determine an effectiveness of nucleating agent.  $N_c$  can be determined as function of cell size and density and is described by equation (7) [20]

$$N_c \cong \frac{1 - \rho}{10^{-4} d \rho_p} \quad (7)$$

Where  $\rho$  [ $\text{g}/\text{cm}^3$ ] is the density of foam and  $\rho_p$  [ $\text{g}/\text{cm}^3$ ] density of polymer matrix and  $d$  acts as a mean cell size in [mm] [20].

Depending on cell size distribution, there are defined mono-; bi- and poly-modal foam structures, respectively. As obviously represented by a simple classification, within mono-modal foams there are only one uniform type of cell size while bi-modal foams are presented by two different sizes or even poly-modal foams are characterized by broad range of cell sizes distribution [20].

## 5 FOAM PROPERTIES

To obtain a homogenous fine-cell structure is necessary to ensure a complete dissolution of blowing agent in a polymer matrix. Otherwise a non-uniformity of a cell structure and heterogeneity of pores will occur, which may also negatively affects a foam surface [4].

Small molecules of physical blowing agent can act as a plasticizer when diffuse between molecules of polymer and distance them, what results in reduction of  $T_g$ . This implies in decrease of solid polymer modulus and liquid polymer viscosity, which directly affects the bubble growth rate. Additional impact on bubble growth is observed in semi-crystalline polymers, where plasticization suppresses crystallization thus bubble growth and its expansion is not interrupted by self-freezing process caused by fast crystallization, which is typical for PE, PP [4].

### 5.1 Physical Properties

When the foaming is finished, the obtained structure should contain required volume level of a gas phase and the maintain stability when subjected to load of final application. Gas and its pressure locked inside the closed-cell foams affects numerous of physical properties such as thermal insulation properties of the foam [7].

Polymer matrix works in a foam structure as a skeleton and it is fulfilled with a gas bubbles. If the prepared foam consists of only two substances, specifically a polymer matrix and voids represented by air, it simply means that most of physical properties, such as melting temperature, are characterized by a solid phase of foamed product.

### 5.2 Density of Foamed Polymers

Apparent density is an elementary parameter, characterizing relative contents of the solid and the gas phase in a material. Density also called a volumetric weight, as a morphological parameter imparts some of basic materials characteristics to the prepared foams like physical properties such as strength, or electrical and thermo-physical properties [2].



Density and density distribution characterize polymeric foams as well as any other polymeric material [20].

Modern foaming technologies produce polymeric foams with densities varying in a wide range from 1,6 kg/m<sup>3</sup> up to 960 kg/m<sup>3</sup> [6]. Therefore, all cellular materials can be divided in a five classes depending on the value of their density[2] :

- A very light materials ( $\rho = 3 - 50 \text{ kg/m}^3$ );
- Light foams ( $\rho = 50 - 200 \text{ kg/m}^3$ );
- Medium-weight materials ( $\rho = 200 - 500 \text{ kg/m}^3$ );
- Heavy materials ( $\rho = 500-700 \text{ kg/m}^3$ ) and;
- Super-heavy cellular plastics ( $\rho > 700 \text{ kg/m}^3$ )

As an ultra-low density foams are classified those with a density lower than 20 kg/m<sup>3</sup>. To obtain such a kind of low densities from 9,6 to 24 kg/m<sup>3</sup> it requires a huge expansion, which can be made up by blending *PO* with elastomer (3 to 30wt%) [4].

Nevertheless, regarding material of choice, there is more simple classification of *PO* foams distinguishing the low density polyolefin foams (up to 240 kg/m<sup>3</sup>) and a high density *PO* foams with a density above this limit [35].

Relative density is a density of foam divided by a density of pure polymer matrix [7].

In practice the density is calculated as a ratio of sample weight  $m$  to geometrical volume  $V_0$  as described in equation (8) [2].

$$\rho = \frac{m}{V_0} \quad (8)$$

However, the general concept of density determination is given by equation (9)

$$\rho = \rho_p(1 - G) + \rho_g \quad (9)$$

Where  $\rho_p$  is the density of polymer phase (ratio of the total material mass to the difference between the total volume of the material and the cell volume),  $\rho_g$  is the gas density in the cells; and  $G$  stands for a foam porosity (ratio of the cell volume to the total volume of material) [2].

Foam density can be controlled by the level of used blowing agent and the correlation between these two parameters is observed. Inverse proportionality characterizes the relation between foam density and *BA* level [35].

### 5.2.1 Density and cell size

There is a hyperbolic function derived from a mathematical model, which describes the relationship between the density and the cell size. After few mathematical simplifications and assumptions that spherical cells in a foam structure with diameter  $d$  form a cellular structure are arranged in a cubic lattice, we obtain an equation (10) defining the density/cell size relation in a small range of densities, if  $\delta$  meaning a wall thickness is a constant[2].

$$\rho = \frac{\pi \cdot \delta \cdot \rho_p}{d} \quad (10)$$

### 5.2.2 Density and wall thickness

$$\rho = \frac{\pi \cdot \delta_{ct} \cdot \rho_p}{d - d_{ct}} \quad (11)$$

Wall thickness cannot be considered as a constant within a broad range of densities, but it is a linear function of the density. Therefore the equation (11) is widen, when  $\delta_{ct}$  is a critical (minimum) wall thickness, still able to support a cellular structure and  $d$  lies between limit values of diameter as stated in equation (12) [2],

$$d_{ct} < d < d_{max} \quad (12)$$

where  $d_{ct}$  and  $d_{max}$  respond for minimal or maximal diameter of stable liquid polymer foam.

## 5.3 Mechanical Properties

Mechanical properties of foams can be measured in a compression mode within a dynamic mechanical analysis, which is mainly used for qualitative measurements of relative soft materials. The sample is placed between flat surface and round-shaped plates of measuring gauge. The lower plate is fixed while the upper plate applies an oscillating force

on a sample to be tested. Compression mode is commonly used to measure modulus of low to moderate modulus materials like foams because the material has some elasticity.

There exists an option how to predict mechanical behavior of open or closed cell foam structures by using a mathematic model. Compressive or tensile modulus equal to compression or tensile strength match with an energy absorption and therefore affects mechanical properties in the term of possible final application. Material's response can be different with respect to the cell type, either open or closed cells, as well as elastic or stretchable type of cell walls. Closed cell foam is characterized as a good energy absorber because of structure and features of every each closed cell. When the wall of cell is stretch and elastic, it dissipates an energy incoming as disturbances [17].

As other mechanical properties are considered rigidity and flexural modulus of foams, important with respect to application performance such as seating, mattresses or packaging, which are determined by polymer type or size of expansion [17].

#### **5.4 Thermal Properties**

Structure of foam consists of polymer matrix surrounding trapped gas inside, but after enough time passed by, the internal gas might be replaced by air due to a concentration gradient. Either gas or air, polymeric foams are classified as thermal insulators. Thermal conductivity and thermal insulation respectively depend on ...and have an opposite meaning. Conduction is under way of convection and radiation

#### **5.5 Acoustic Properties**

Open cell foams are with advantageous used for sound absorbing applications. A sound waves travel across the open cell structure meanwhile leaving traces is diminished and decelerated by reflecting from an internal surface of open cells. In this manner, special properties are bestowed to open cell foams to cushion a noise, especially with a short wavelength and high frequency. The ability to reflect sound waves belonging to energy wave is a material characteristic and depends on every single type of polymer [17].

## 6 GENERAL CONCEPT – FOAMING TECHNOLOGIES

Fundamental transport properties of polymer matrix, or more precisely, way and rate of transport of gases in polymer medium, affect solubility and diffusivity of gases, which depend on morphology, and nature of polymer medium including rubbery or glassy state or crystallinity content [4].

It was assumed theoretically in 19<sup>th</sup> century, that the gas permeation throughout a membrane is combination of diffusion and dissolution (sorption) defined as a gas uptake by polymer. Henry's law described as

$$S = \frac{c}{p} \quad (13)$$

Where  $S$  is the solubility coefficients, which at equilibrium and ideal sorption is a function of the concentration of gas adsorbed per unit mass of polymer ( $C$ ) and gas pressure ( $p$ ). Henry's law constant ( $S$ ) may alter according to  $C$  and  $p$  increase [4].

Polymer chain morphology, mobility and packing affects the transport of a gas in a polymer also with the respect to solubility below or above glass transition temperature  $T_g$ . In amorphous polymers above  $T_g$  the sorption of a gas take after gas solubility in liquids and is sufficiently described by Henry's law. An ideal solubility occurs within atmospheric pressure while both positive and negative deviations occur under high gas pressure. Whereas below  $T_g$  in glassy state of polymer, there is equilibrium, two kinds of molecules differing within gas sorption and transport. Henry's law describes the population with higher diffusion mobility while population of restricted diffusion mobility follows Langmuir isotherm. The difference is caused by two various methods explaining the gas solubility in polymer. During a Henrian process the polymer subjects to distancing of chains by gas molecules which are then placed between the chains. Langmuir contribution to solubility is represented by the surface adhesion of the gas in the small voids in a polymer [4].

Among other important aspects affecting gas solubility and transport, belong degree of cross-linking, crystallinity content and addition of plasticizers and fillers. Density may affects a transport properties when increases the number of polymer side chains which reduces segmental mobility as well as the increase cross-linking degree resulting in

decrease of diffusion coefficient. Equally the decrease of densification and branching, what transforms polymer in a rubbery state, leads to a decrease of a solubility a vice versa [4].

Transport of a gas in polymer takes place in amorphous phase confirming the fact that crystalline phase acts as a barrier for transporting gas. Essential processes of solution, diffusion and transport of gases in polymers, are presented with prediction models. Sorption follows Henry's law therefore the solubility coefficient of the gas in amorphous phase  $S_a$  depends basically on the volume fraction of amorphous phase  $\varphi_a$

$$S = \frac{S_0}{\varphi_a} \cdot S_a \quad (14)$$

Where  $S_0$  is apparent solubility obtained experimentally and means the weight of dissolved gas per unit weight of composite [4].

Diffusion follows Fick's law within temperatures above the  $T_g$  of the polymer. Diffusion coefficient describes the process of diffusion of gas through the polymer and is affected by  $\tau$ , geometric tortuosity parameter defining the distance between crystallites, which thus determine the path of gas in semi-crystalline polymers. When corrections are applied then diffusion coefficient is defined as: [4].

$$D_a = D_0 \cdot \tau \cdot \beta \quad (15)$$

Where  $\beta$  is the chain immobilization factor comprising the fact of lower flexibility of chains which are closer to the crystallites when compared to chains laying within the amorphous fraction [4].

Therefore, the crystalline content affects the solubility and diffusivity of a gas in semi-crystalline polymers as showed in a table (1) below [4].

Table (1): Solubility and Diffusivity of various gases in LDPE and HDPE [4]

Diffusivity ( $\times 10^6$ ) [ $\text{cm}^2/\text{s}$ ]							
	Density [ $\text{g}/\text{cm}^3$ ]	He	O <sub>2</sub>	Ar	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
LDPE	0,914	6,8	0,46	0,36	0,372	0,320	0,193

HDPE	0,964	3,07	0,17	0,12	0,12	0,093	0,057
Solubility (x10 <sup>6</sup> ) [cm <sup>3</sup> (K; 1,013.10 <sup>5</sup> Pa/cm <sup>3</sup> xPa)]							
	Density	He	O <sub>2</sub>	Ar	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
LDPE	0,914	0,544	0,472	0,571	2,54	0,288	1,13
HDPE	0,964	0,028	0,18	1,1	0,22	0,15	0,51

Since fillers are favorably adding to plastics to reduce the price, and plasticizers to improve their processability, there were many studies carried out to obtain resulting effect of additives on foaming process of polymers. There are fillers impermeable to gases and reducing the solubility and diffusivity, however in general the addition of filling agents decreases the ability of the gas to permeate through the continuous polymer phase, and not depending on type of filler, or pigment, respectively, whether it is platelet (like clays) or spherical such as titanium oxide [4].

## 6.1 Mechanical Foaming

Mechanical way of foaming comprises of introducing a gas directly inside the material to be foamed since the air is whipped in the solution [6]. Various gasses can be feed in to the polymer matrix, such as air, nitrogen, carbon dioxide, hydrogen, ammonia or helium at atmospheric pressure [2].

As important example is named a latex frothing [6] or mechanical foaming of silica in a sol-gel state was studied [39]. To provide a mechanical foaming there can be employed a mechanical foaming agent which is inactive to foamed material [40]. To avoid a harmful CO<sub>2</sub> generation and non-ecologic foaming agents such as Freon, is the main aim of using this process.

## 6.2 Physical Foaming

Preparation of foam by physical foaming process means that the melt is simply saturated by gasses and might be directly extruded or injected in a mold. However, inert

nucleating agent helps to prove gas distribution and create a finer structure. Endothermic and exothermic ways of nucleation are usually described [17].

A physical blowing agent saturates the polymer matrix at a certain temperature and pressure and forms a cellular structure while escaping from polymeric melt due to a sudden thermodynamic change (temperature increase or a pressure drop). Created foam structure is characterized by cell size, density and soft or rigid properties depending on a membrane, which forms the cell wall. Whether the membrane ruptures or not there is generated open or closed-cell structure [4].

### **6.2.1 Direct gassing extrusion**

Foam extrusion with an additional gas represents a simple technology of physically foamed light-weight materials [17]. Simple extrusion process is usually used because of its economic advantage. A volatile organic blowing agent is injected inside an extruder where is mixed onward homogenously with a polymer melt. Specifically, with LDPE it is the most widely used because of their adequate solubility in a polymer met [35]. Atmosphere gases such as nitrogen, carbon dioxide and even air, or also gases produced in petrol branch, namely pentane, propane and butane are directly pressed into the extruder to blend with a molten polymer, where as a *PBA* should build a complete mixture. Moreover the chemical function of added gas acting as a plasticizer, allows to reduce the processing temperature [17]. The mixture is cooled to the lowest possible foaming temperature after blending the gas with a molten polymer, and the cellular structure forms itself due to a decompression of melt [35].

When choosing a foaming gas there are many aspects and requirements including non-combustibility and suitable solubility of a gas. Next conditions are a low molecular weight and gas's inertness. As far as health aspects, elected gas should not be toxic and health or environmentally harmful and of course the question of a price is very important nowadays [17].

Equimolar blend of sodium bicarbonate and citric acid is a new development in a physical blowing nucleation. After reaction between bicarbonate and acid there are many

decomposition components acting as a spot place of bubble formation. An example of its utilization is direct gassing and extrusion of polystyrene or LDPE [17].

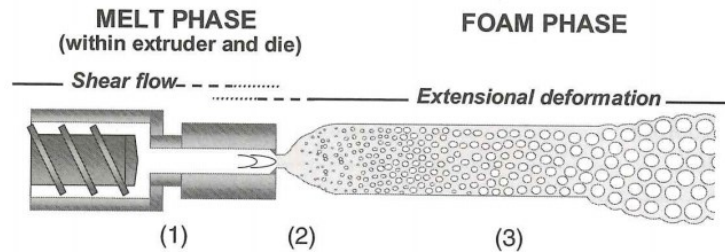


Figure (9): Extrusion foaming process.

Figure (9) describes an extrusion process of foaming [4]. In the first section (1) a single-phase polymer melt already laded by gas is pumped toward die exit. (2) Large pressure drop evoke a bubble nucleation. (3) Cells expand and cellular structure stabilizes because of cooling of polymer melt.

### 6.2.2 Direct gassing injection molding

Common injection mold machine with a screw piston is used to produce foams. Gas is coming to the extruder through a barrel directly in the molten polymer. Expansion occurs when the polymer is injected and the gas is sufficiently dissolved in a material. Continuous layer on the surface is generated and thus foams are called structural foam because of its integral surface [17].

Injection molding offers the possibility to use nucelants in the same way as in the extrusion process. Precisely distributed foaming gasses allow to generate lower pressures and thus aluminum based molds are sufficient for direct gassing injection molding and therefore are often used for production of larger parts with high weight [17].

### 6.3 Chemical foaming

Chemical way of foam preparation stays at a first place in a foam market especially in non-food applications. CBAs are favored and widely used to foam all thermoplastic polymers. A special attention is paid on Azodicarbonamide (ACA) because of its advantages



coming from its suitability not only with cross-linked polyethylene but also with ethylene vinyl acetate which the ACA is the most applicable with [17].

Different methods of chemical foaming are available as described below. Conventional injection molding method allows a direct addition of CBA into hopper while within an extrusion the [17].

### **6.3.1 Extrusion**

Suitable gas decomposing in the range of processing temperature and has a proper solubility in the polymer melt. Decomposition product liberated within a gas disintegration should not affect a final foam in any negative meaning such as color, toxicity or influence on environment [17]. First of all the decomposition temperature of a foaming agent must be reached in extruder and secondly the high pressure must be kept instantly to retain a dissolved gas within the polymer substance [17].

### **6.3.2 Expansion**

Essential steps of foam extrusion with the CBA are composed of sheet production, cross-linking and foaming. Depending on chosen production process and desired parameters, the chronology of each step may vary. However, the basics of expansion method rely on the melting temperature of the polymer  $T_m$  and the decomposition temperature  $T_d$  of the blowing agent. First, the blending takes place at a temperature above  $T_m$  but below  $T_d$ , to ensure a homogeneity of blend and to perform the process of cross-linking which shall be completed before the  $T_d$  is reached. Finally, the foaming temperature ( $T_f$ ) is supposed to exceed the  $T_d$ , however there is an effort to keep  $T_f$  as low as possible to avoid potential thermos-oxidative degradation of polymer [35].

## **7 ADDITIVES**

### **7.1 Nucleating agents**

Polymer foaming by usage of nucleating agents provides to reach a finer cellular structure and lighter weight of final foam [17]. Nucleating agents, such as porous minerals, indicate a bubble formation, as far as they are homogeneously dispersed in a gaseous phase. Small particle of talc for instance, give a huge area furnished by its surface, where a bubble growth leads to start so bubble size distribution can be controlled and refined [17]. Different minerals are used within physical foaming besides the already appointed talc; there are also calcium carbonate or silica.

Several substances work on a principle of endothermic systems are commonly used in a physical foaming process, furthermore they can act as chemical foaming agents. There are organic fruit acids (citric acid, lactic acid, oxalic acid), carbonates (bicarbonates,  $\text{KHCO}_3$ ,  $\text{NaHCO}_3$ ) and inorganic non-fruit acids (boric acid), ranked in this group of nucleating agents [17].

### **7.2 Blowing Agents**

The purpose of blowing or foaming agents is to produce a foam structure or expanded plastics. Resulting pores can be completely enclosed or interconnected. Among the main advantages of cellular plastics are their high strength/weight ratio and earlier mentioned excellent insulating properties [19].

There are two basic principles of usage of blowing agents, founded on processes of dispersion and condensation. Foams prepared by dispersion method are created with gasses, in comparison to foams produced by condensation method in which the blowing agent is employed [41].

In general, there are classified physical and chemical blowing agents (PBAs, and CBAs, respectively) regarding the mechanism of gas liberating within the compound [41]. CBA mostly in a form of powder mixed with a polymer even before the foaming process starts and its adequate solubility and diffusivity are two fundamental aspects for successful CBA

usage. On the other hand there are PBAs, generally in the form of liquids [41] and their main benefits are prioritized within a conventional way of foam extrusion because of their high level of expansion and moreover they are profitable from an economical point of view [17].

Blowing agents are characterized by parameters describing the initial temperature of BA decomposition; amount of released gas in  $\text{cm}^3$  (at unit time 1 min and within consumption of 1g of BA); pressure developed by the liberated gas; and the rate and kinetic of a gas liberation [41].

### **7.2.1 Physical Blowing agents**

As mentioned above, group of physical blowing agents consists of gases, solids or liquids such as pentane, PBA-sorbents, low-boiling liquids [41] or carbon dioxide ( $\text{CO}_2$ ), which is a popular physical foaming agent due to its low cost and environmental friendly behavior [4].

PBA are sometimes distinguished with respect to ozone layer depletion, to halocarbon blowing agents like  $\text{CCl}_3\text{F}$  (trichlorfluormethane) and environmentally more welcomed zero-ozone layer depletion BA such as low hydrocarbons (ethane, propane, butane, pentane), hydrofluorocarbons and inorganic compounds (water, carbon dioxide) [35].

During a physical blowing, the gas is liberated within a physical processes such as evaporation and desorption under the conditions of elevated temperatures or pressure drop, whereas PBA itself does not subject to chemical reaction and thus any chemical changes [41].

Suitable PBA should be under the pressure easily dissolved within a chosen polymer. The parameter of BA profitability is the rate of permeation through the cell walls. Basically, the BA should permeate slower than air to avoid a unfavorable phenomenon of polymer foam shrinkage during aging [35]. Moreover, the desired BA should meet requirements on non-flammability, non-toxicity or at least a low-flammability, low-toxicity and a low cost. [35].

## 7.2.2 Chemical Blowing Agents

Chemical blowing agents are grouped into the most widely used blowing agents, which among them belong those working differently such as compounds liberating gaseous product as a result of reversible equilibrium thermal decomposition or as a result of irreversible thermal decomposition. Another principle of gas liberation is a chemical reaction between two components of a foaming mixture [41].

Application of CBAs are ascribing two main advantages. Firstly, they are easily processed with regular instrumentation and thus no special equipment is needed and secondly, it is easy to compound them with a material to be foamed [41]. Additionally, in some cases, *CBA* can be used as a nucleating agent for *PBA* instead of talc with advantageous of no residue remaining in a foam due to volatility of *CBA*, so it allows to control a nucleation of recycling and reusing material [17]. On the other hand, although *CBA* belongs to reactive agents, there is an expressive disadvantage. As a main inconvenience is called its low solubility in thermoplastic polymers, which is much lower than for organic gasses [17].

When choosing an adequate *CBA* there must be followed few requirements such as the decomposition temperature of *CBA* must be similar to melting temperature of foamed polymer. The *CBA* decomposition should not produce a heat to avoid a thermal degradation of foamed polymer. Other requirements are imposed on released gas, which should be nonflammable and non-toxic and its liberation must course in a small temperature range. In general, the polymerization process of foamed material must not be influenced by any component of *CBA* system [41].

Figure 10 [4] pictures the relation between *CBA* and gas molecules with respect to time and temperature increase. (a)  $T < T_{\text{onset}}$ ; (b)  $T = T_{\text{onset}}$  characterized by low viscosity zone around residual particles which is presented due to enhanced plasticization; (c)  $T > T_{\text{onset}}$  where gas molecule diffusion and homogenization is observed.  $T_{\text{onset}}$  responds to the temperature when *BA* starts to decompose.

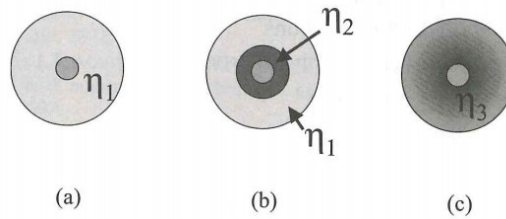


Figure (10): CBA decomposition and gas molecules diffusion with increasing temperature and time.

In the course of CBA decomposition, it releases inorganic gasses like carbon dioxide or nitrogen, respectively, when endothermic, and exothermic system, respectively, is used. Exothermic group of CBA has a higher foaming efficiency ( $220 \text{ cm}^3/\text{g}$ ) in comparison with an endothermic one ( $120 \text{ cm}^3/\text{g}$ ) [17].

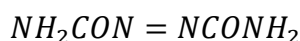
There is no perfect or universal blowing agent suitable for all substances; however, there are two major groups distinguished on exothermic and endothermic systems. The one between above-mentioned are called enexothermics and contain mixture of one endo and one exothermic blowing system [17]. Advantages of using an exothermic can be consider ease blending and handling, its range of decomposition temperatures. Nevertheless, relevant disadvantages are noted, that exothermic are not allowed for food purposes, there is a smell generated while using and they can cause a discoloration of final product. As the example of exothermic BA can be mentioned sulfohydrazide, hydrazide and tetrazoles, while sodium borohydride is an example of exothermic system.

ACA as an exothermic system may generate a significant surface roughness. To compare exo and endo, with respect to the developed gas pressure during its decomposition, it is noticeable higher, when exo ADC is used than with endo is. This can cause differences in a bubble size distribution and physical properties, consequently, affecting a weight reduction and so there is an influence on the cooling time [17].

Endothermics have some drawbacks in comparison with exothermics, however they are suitable for use in food applications as well as in a pharmaceutical and cosmetics applications. Due to its slower decomposition within polymer matrix there is a better distribution [17].

Regarding the requirements described above, Azodicarbonamide was chosen as a CBA in this study. ACA belongs to organic blowing agents, which means that the reaction of gas liberation is irreversible and by-products of BA decomposition can decrease the polymer thermal stability because of induction of plasticizing effect. Moreover, the cost of organic BA is higher and some of them are represent as toxic substances [41].

Formula of ACA:



ACA from the class of azodicarboxylic acid derivatives is the mostly often used nitrogen-releasing compound used for a blowing of polyolefin foams. There are several reasons to this, namely the characteristics such as decomposition temperature, toxicity, rate of gas release, gaseous composition and its cost. Its  $T_d$  lies between 190–240 °C, however by adding an activator the temperature can decrease to approximately lower than 130 °C. Released gas consists of nitrogen and carbon monoxide what has a positive impact on foam shrinkage suppression. ACA is one of the most effective blowing agents because of its gas number equal to 230–270 cm<sup>3</sup>/g or even more up to 430 cm<sup>3</sup>/g in interaction with catalyst. Therefore, ACA is often used with cross-linked materials with sufficient melt strength. Another advantage is an incombustible or rather self-extinguishing, which plays in aid of ACA beside other organic blowing agents. Hence ACA is recommended to use for a foaming polyolefins and other polymers like polyvinylchloride, polyamides, rubbers, epoxides and acrylates polymers [35, 41]. This study made the account of stability of ACA, which remained sufficiently within a chemically neutral polymer matrix.

### 7.3 Activators

As it was mentioned when describing a principle of CBA function, there are available substances effectively used as activators of CBA. Activator catalyzes and accelerates the decomposition of blowing agent and in addition, changes an amount of released gas. Among the activators used in relation to ACA there are transition metals (cadmium, zinc),

urea, polyols and organic acids. The widely used with ACA are zinc stearate and zinc oxide ( $ZnO$ ) also employed in the experiment of this study [35].

On the other side of activators there can be applied inhibitors suppressing the decomposition of blowing agent like phenols, amines and acid hydrazides for ACA.

## 7.4 Crosslinkers

Cross-linking, as mentioned above, stabilizes the structure to be foamed, moreover it protects the cellular product against eventual thermal collapse. Among the cross-linkers suitable for cross-linking of polyolefins are ranked peroxides like butyl-cumyl peroxide or di-butyl peroxide; multifunctional azides or an organo-functional silane [35]. As another option how to achieve a cross-linked polymer chains can be considered usage of a high energy irradiation like X-ray, gamma-radiation [42] and high energy electron beam [37, 38], [24] or a moisture cross-linking, which is ensured by a silane cross-linking technique [43].

Melting point of base polymer matrix should be taken into account while selecting adequate cross-linkers, therefore LDPE with  $T_m$  between  $100^{\circ}\text{C}$  and  $120^{\circ}\text{C}$  is in suit with dicumylperoxide (*DCP*), which is commonly used [44].

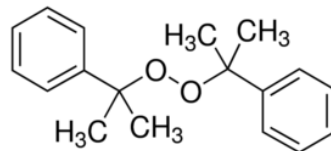


Figure (11): The chemical formula of dicumyl peroxide

Figure (11) shows the schematic illustration of DCP used as a cross-linker in this study, which has a decomposition temperature  $171^{\circ}\text{C}$  and  $115^{\circ}\text{C}$ , respectively in one-minute and ten-hour half-lives [35].

Optimum cross-linking provides the greatest possible volume increase while no ruptures is present. To gain such performances it is important to care about dosage of cross-linking agent and molecular structure of polymer (density, length of branching and molecular weight distribution). Chemical description of crosslinking polymer by using a peroxide Figure (12) [45]:

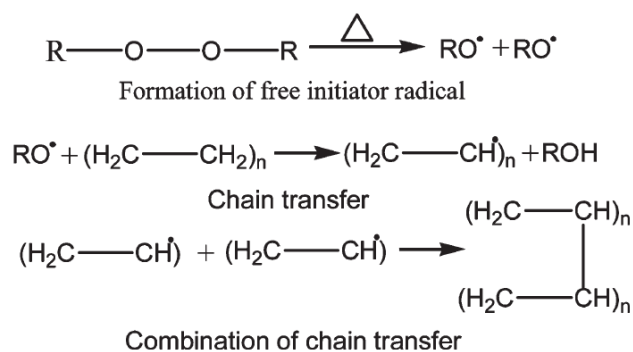


Figure (12): The chemical mechanism of polymer chain cross-linking reaction.

## 7.5 Flame Retardants

Combustion properties of polymeric foams and their ignition are very important social and economic problems. The possible solution is a challenge of understanding interdependence between macromolecular and morphological structure of polymeric foams. Hence, the difference between non-foamed materials and hetero-phase systems of foamed polymers is significant. Evidently, the response of foams to external heat sources can develop in a dangerous reaction because of potency of energy storage in their surface. In general, foams are easy to ignite, the fire propagate very quickly and there usually occur a smoldering combustion. In account of all the previous mentioned reasons, it is obvious, that the feasible solution is of interest in that field of polymeric foams [29].

Polymers are in a most cases flammable materials because of their organic origins and thus there are parameters like Limiting oxygen index (LOI) describing this technical issue and defining the minimum volume percent of oxygen concentration in nitrogen, which is needed to support a combustion of testing material. Since ambient air contains 21% of oxygen, there are classified a self-extinguishing polymers with an LOI higher than 0,21. There are few flame retardants usually used to prevent combustion of product such as halogens (bromine, chlorine, phosphorous) [19]. Nowadays the trend of eco-friendly non-halogenated or halogen-free flame-retardants is becoming more popular. Polyethylene has a LOI 0,18 and as a typical flame retardant to be chosen in mixture with PE can be mentioned chlorinated paraffin [19].



Porous materials are composed of a matrix material forming a walls and ribs of the structure and of course, of a huge amount of free space filled out by a gas. To initiate a combustion of this gaseous phase there must be reached a critical temperature ( $T_i$ ) (ignition) of a surface of organic surroundings. Both flame combustion and smoldering are developed within a porous material combustion [29].

Recent developments in a non-flammability of polymeric foams offer a several possible solutions such as advancement in new highly thermally stable polymers or blending with such many fillers working as a barrier or blockers as well as improved properties of additives and flame retardants [29].

## 8 APPLICATIONS

There are several tailored applications regarding the chemical nature of used polymer. Usually, essential classification covers specific segments of industries like food (*PET* or *PLA* sheets for food packaging), medical segment, astronautic and aviation. The rest of wide range of applicability of polymeric foams is not so strict and straightaway so many industries include foamed product as far as main characteristics like density, thermal conductivity, Young's modulus and strength as described in the Figure (13). Among commonly used chemically foamed extrudates belong rigid PVC foams, PVC sheets, profiles and pipes. LDPE and HDPE foams are with favor used for cable insulations and sealants. Foamed PP for thermoformed food packaging are additionally applicable in microwave heating [17].

The range of applicability of polymer foams compared to other solid materials is presented in the Figure (13) [20].

With respect to the type of foams if they are flexible or semi-flexible, respectively and rigid there is a huge field of applications. Strong representation of semi-flexible and flexible foams is in industries such as furniture, bedding, transportation, shoes, toys and packaging. On the other site, the rigid structures found application in building and construction segment, containers for food, flotation or appliances [6].

Usually, the high-density PO foams have founded their utilization within a wires, cables and structural purposes, while low-density PO foams are useful in the field of cushion packaging [35].

Closed-cell polyolefin foams shine at a low water absorption just due to a closed pores of cellular structure, as well as at no dust absorption [38].

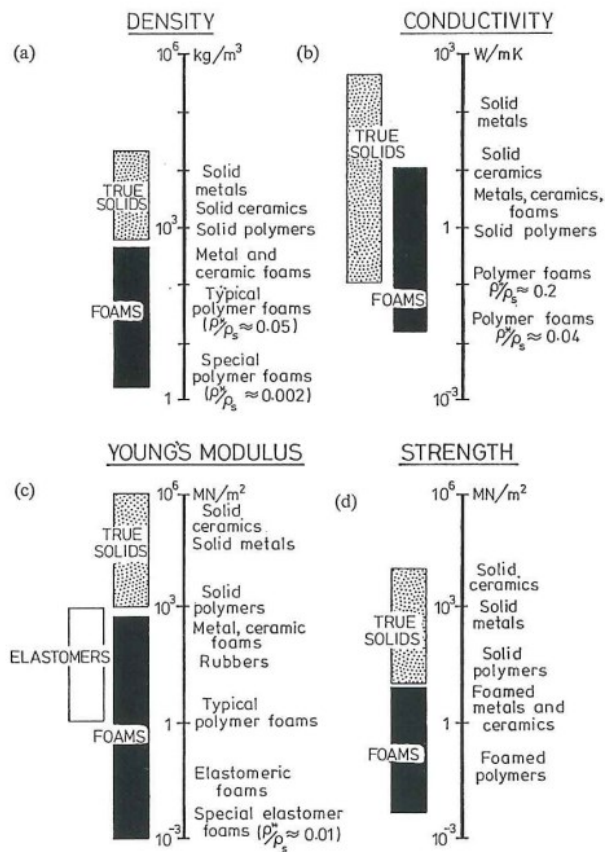


Figure (13): comparison of (a) density and physical properties (b) conductivity; (c) Young's modulus; (d) strength of polymer foams and other materials.

Characteristics and properties bringing along suitable for each applications are considered resiliency, ease fabrication, energy absorption and low thermal conductivity of polyolefin foams [35].

## 8.1 Thermal Insulation

Low thermal conductivity of polyolefin foams leads to idea of thermal insulation applications, moreover a sufficient elasticity and flexibility of foam products allow to thermally insulation of curved surfaces. Therefore, insulation of pipes are widely assured by manufacturing directly the tube-shape foamed product. Among other insulation properties belong gaskets or grommets [35].

Thermal conductivity of foamed plastics can differ even when almost all conditions stay the same, including density or chemical composition. This can be caused by a different

cell size of final foam giving a different path of heat flow by radiation and convection. Hence the increase of cell size leads to increase of thermal conductivity coefficient of measured foams [20]. There are described several mechanism of heat transfer taking place in porous materials such as conduction through both gas and solid, convection through gas, and radiation between the gas and solid interface [3].

This method is useful when characterizing materials generally using in building industry, electronics and aerospace or cosmic industry. Materials suitable for those applications are required to have a good thermal stability and low thermal expansion [38]. Example of material suitable for these applications is LDPE with thermal conductivity around 0,33 [19].

## **8.2 Acoustic insulation**

Sound insulation and low dynamic stiffness suit with a polyolefin foamed products. Generally, cellular structure conforming the acoustic properties is thought the open-celled one. However it was developed that even closed-cell insulate the sound very well if the cells reach large sizes and thus the membrane mechanism of acoustic insulation works [35].

Álvarez-Láinez et al. have investigated open-cell PO-based foams and obtained a very high absorption coefficient even higher when compare to results of PU foams [46]

## **9 METHODS AND MEASUREMENTS**

### **9.1 Blending**

A polymer blend is a mixture of two or more polymers. The aim of blending two polymers is most often improving the processability of the base material, which answers that rationale for blending is improving material performance and economic advantages for manufacturers. In this way, we consider 2wt% of addition as a blending while the lower percentage acts as additive [4].

### **9.2 Compression molding**

One-step and two-steps compression molding are usually distinguished. In a one-step molding the blended compound as a homogenous mixture of polymer matrix, blowing agent and cross-linking agent is inserted to a mold [35]. When heat and pressure are applied, the blowing agent starts decomposing and the cross-linking agent cross-links a polymer chains therefore the foam expansion runs. In two-steps, molding the mixture of components to be foamed is firstly heated and expanded only partially, in contrast to one-step molding. The break between two steps is assured by quenching the compound. Second step of heating and expanding takes place at atmospheric pressure [35].

### **9.3 Thermal conductivity analyzer**

Non-destructive thermal testing instrument providing a thermal characterization of thermal conductivity and thermal effusivity. Basic principle works on method of modified transient plane source technique. Measurement takes place on a one-sided, interfacial heat reflectance sensor, which applies a quick pulsating impulse (momentary constant heat source) on the sample. The applied current is known and it is equivalent to applied amount of heat. The response of material provides a direct way of measuring thermal transfer properties because of inverted proportionality between thermal conductivity and rate of increase of the temperature between the sensor and the sample [47].

## 9.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) belongs to methods of thermal analysis working on a principle of measurement of difference in amount of a heat required to increase a temperature of both sample and reference. The examined heat difference is measured as a function of temperature. The specimen is placed in to a crucible while reference have a defined heat capacity over the range of temperatures to be measured. The physical transformations of a sample such as phase transition from solid state to molten (liquid) phase or crystallization, respectively, needs a certain amount of heat to add or withdraw, respectively, due to an endothermic (exothermic respectively) process in comparison to the reference sample. Examination of polymeric materials is basically provided in order to determine their thermal transitions such as glass transition temperature, melting temperature or crystallization temperature. Seeing that the  $T_m$  of polymers depends on its molecular weight and thermal history, and they are tabulated in literature, there are more applications of DSC measurements, widely used to determine a polymer degradation or crystalline content, watching the shifting of curves or changing of peaks. Figure (14) shows a scheme of measuring system [48]

- 1, Furnace lid
- 2, Crucibles on DSC sensor
- 3, Silver furnace
- 4, PT100 of furnace
- 5, Flat heater between two insulating disks
- 6, Thermal resistance for cooler
- 7, Cooling flange
- 8, Compression spring construction
- 9, Cooling flange PT100
- 10, DSC raw signal for amplifier
- 11, Purge gas inlet

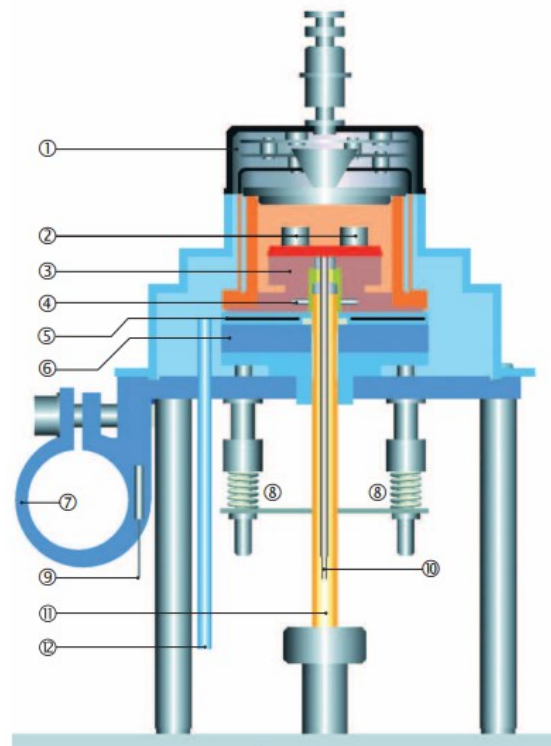


Figure (14): Scheme of DSC measuring system

## 9.5 Scanning Electron Microscopy

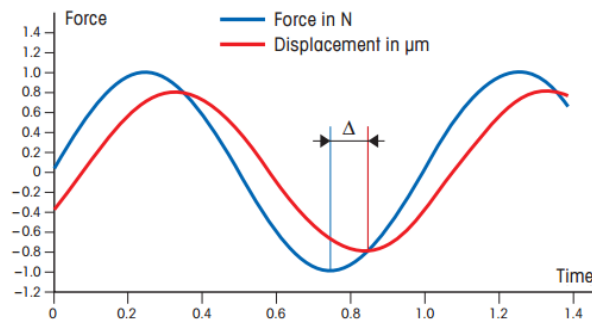
Closer inspection of cell morphology was investigated using a scanning electron microscope. Specimen is probed with a focused electron beam causing an interaction between surface of the sample and incident electrons, which results in energy losses. These are converted into a heat, light emission, X-ray, high-energy backscattered electrons or low-energy secondary electrons similarly as was utilized in this thesis. Therefore, SEM provides to study topography or composition of a sample surface.

## 9.6 Dynamic Mechanical Analysis

Good mechanical properties of prepared foams are required for some of already mentioned applications [38]. Viscoelasticity of cell walls and the density of foam significantly influences the recovery of polymer product such as sports mats [21].

The principle of Dynamic mechanical analysis (*DMA*) is measuring of displacement amplitude (material's response) induced by oscillating force acting on the testing sample. Derivation of the time lag ( $\Delta$ ) between the two curves obtained from measurement, shown in the Figure (15), results in the phase shift ( $\delta$ ) between the force and displacement signal, which can be calculated from equation (16) [48]

$$\delta = 2 \cdot \pi \cdot f \cdot \Delta \quad (16)$$

Figure (15): Force and displacement at a frequency  $f$ ,  $\Delta$  time delay

It allows to calculate a properties like viscosity, describing a tendency of material to flow, and a modulus characterizing a stiffness of material [49]. Damping responses to ability of the material to loose energy as a heat and elasticity and ability to recover from deformation [49].

The characteristic parameters describing the DMA measurement, are complex modulus  $E^*$  (given by storage  $E'$  and loss  $E''$  moduli), and the phase shift between force and displacement signals [48]. The modulus is calculated from the applied force amplitude ( $F_A$ ), the measured displacement amplitude ( $L_A$ ) and the phase shift.  $E'$  is related to energy stored elastically and reversibly while  $E''$  relates to energy transformed into heat and irreversibly lost. Both storage and loss moduli can be determined from measured stiffness ( $S$ ) and the geometry factor ( $g$ ).

Equations (17-20) are applied.

$$E' = |E^*| \cos \delta \quad (17)$$

$$E'' = |E^*| \sin \delta \quad (18)$$

$$\tan \delta = \frac{E''}{E'} \quad (19)$$

$$|E^*| = S \cdot g = \frac{F_A}{L_A} \cdot g \quad (20)$$

Elastic  $E'$  modulus and imaginary  $E''$  modulus are calculated from the response of material to applied sine wave by using a knowledge of measured phase angle (figure - ) and amplitude of the signal [49]. As a damping is defined the ratio of imaginary and elastic moduli which reply to the ability of material to return energy ( $E'$ ) or to lose energy ( $E''$ ).

The modulus is temperature- and stress-dependent and can predict how the material will behave in real conditions. Indeed a modulus changes and drops dramatically within a range of temperatures when material passes through a transition temperatures like glass transition temperature [49].

By using DMA there can be characterized material's properties with respect to the response to vibrations and the energy dissipation capabilities. Polyolefin foams as a viscoelastic



materials dependently respond to the force and compression rate [22]. Additionally, other parameter can be determined such as crystallization and melting, glass transition and phase transformations . Low frequency and a low compression range belong to elementary parameters required for insulating purposes [9].

- 1, LN<sub>2</sub> inlet/outlet
- 2, Heater element
- 3, Sample holder
- 4, Sample
- 5, Drive shaft
- 6, LVDT displacement sensor
- 7, Drive motor
- 8, Drive shaft guidance (spring)

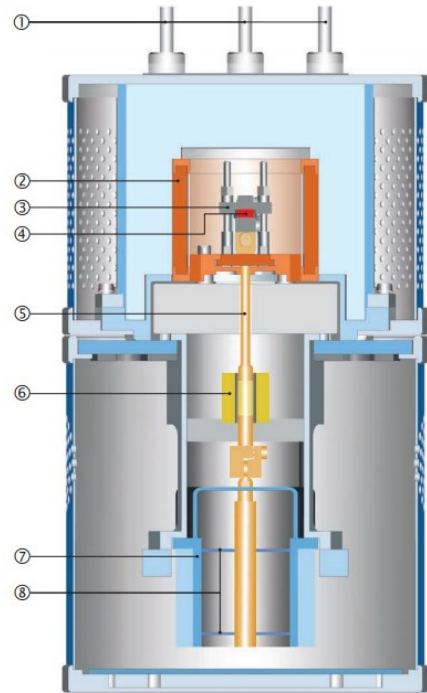


Figure (16): Scheme of DMA measuring system.

Figure (16) pictures the scheme of DMA measuring system used in this study.

## 10 ENVIRONMENTAL ASPECTS

New developments in polymer materials as well as modern technologies of foam processing have helped to put foams forward to the fore of its usability. However, many advantages of polymeric foams allow producing fast and cheap tailor-made products, which results in expressive increase of consumption and therefore a waste production. There are already applied several environmental regulations such as Kyoto protocol known as an international treaty that commits to reduce a greenhouse gas emissions including a carbon dioxide, in developed countries to avoid or reduce an environmental impact of high material consumption [17]. The main disadvantage is given by a short life cycle of products and poor knowledge of recycling, re-using or re-manufacturing of once manufactured product.

Another issue is a chemical matter of the blowing agent. There already exists an effort to reduce some of them such as stable halogenated brominated and chlorinated hydrocarbons by assessment of special taxes when using them. The main reason of reduction of hydrochlorofluorocarbons and other blowing agents is depletion of ozone layer [17]. Many environmental aspects have led to new developments in alternative of blowing agents. One of the most discussed is a depletion of ozone layer inflicted by the presence of chlorine and bromine in the stratospheric layer [4].

To save energy and exhaustible resources there should be further investigations on sustainable sources, which are recyclable (compostable or water-soluble). As a good example of green substitution serves degradable foams made of sustainable sources like Polylactide acid (*PLA*), corn, green plants. These can help to solve the issue regardless increasing price of gasoline, petroleum and raw materials needed for polymers such as bisphenol A and benzene. in the future.

Cellular plastics made of Polylactide/Polyolefin blends, were studied recently. Polylactide belongs to biodegradable, biocompatible and bio-renewable polymers widely used in commercial products. Preparation a foamed PLA material containing voids brought such an advantage of material and thus a cost saving. There were prepared closed-cell structures on the base of PLA by uniaxially stretching at a room temperature. Another

additives such as polypropylene or epoxy-functional terpolymer were blended in this study to prove the mechanical properties of PLA foams (tensile strength) [36].

Advantageous position of biological sources lies in their fast and easy degradability of products according to its decomposition in natural environment. Among polymers decomposing under the influence of moisture, heat or UV radiation are ranked PLA, Polyvinylalcohol or Poly caprolacton [17].

## **II. ANALYSIS**

## 11 EXPERIMENT

### 11.1 Used Materials

LDPE elongation viscosity behave a strain hardening under the high value of strain rate while very small or no strain hardening appears when small strain rate is applied. Magnitude of strain hardening of polymer chains depends on a content of long chain branches. In general, rheological behavior of polymer melt and thus also the strain hardening underlines to the chain characterization such as number of branches, their architecture and the length distribution [4].

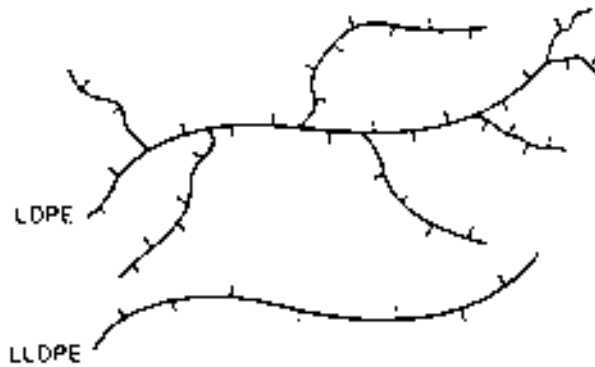


Figure (17): Schematic illustration of LDPE and LLDPE polymer.

#### 11.1.1 Polymer Matrices

LDPE with the density  $922 \text{ kg/m}^3$ , LLDPE (Borstar<sup>®</sup> FB2230, QUEO<sup>™</sup> 0201, QUEO<sup>™</sup> 8201) were supplied by Borealis, (*Austria*). LLDPE with controlled length of side chains respond to ethylene based octane-1 (or butane-1, respectively) plastomer, which were produced in a solution polymerization by using a metallocene catalyst.

The acronym, density, length of side chains, chemical composition and producer of materials used in this investigation are tabled in Table (2). Describing foamed samples are composed of LDPE (low-density polyethylene) matrix in 90%, 85% and 80% and LLDPE with a different densities and different length of side chains were added in 10%, 15% and 20% contents.

Table (2): Characteristic parameters of used polymeric materials.

Sample	Acronym	Density [kg/m <sup>3</sup> ]	Number of carbons in side chains	Composition	Producer
FA 3221	LDPE	922	-	LDPE	Borealis, Austria
Borstar® FB2230	C4-1	923	C4	LLDPE	Borealis, Austria
LLDPE LL 1001	C4-2	918	C4	LLDPE	ExxonMobil™, USA
QUEO™ 0201	C8-1	902	C8	LLDPE	Borealis, Austria
QUEO™ 8201	C8-2	883	C8	LLDPE	Borealis, Austria
Polymer Blends					
Blend	Ratio	Composition			
LDPE/C4-1	90/10	90phr* LDPE + 10phr LLDPE			
LDPE/C4-2	85/15	85phr LDPE + 15phr LLDPE			
LDPE/C8-1	80/20	80phr LDPE + 20phr LLDPE			
LDPE/C8-2					

\*(Phr) = per hunderet resin.

The same PO composition of prepared foams is counted as a huge advantage in practical recycling procedure [38]

### 11.1.2 Additives

Azodicarbonamide 97% produced by Sigma Aldrich, (USA) was used as a blowing agent in the amount of 8 phr in all cases.

Dicumyl peroxide or bis(1-methyl-1-phenylethyl) peroxide in 98% with M<sub>w</sub> (molecular weight) = 270,37 g/mol obtained from Sigma Aldrich, (USA) was employed as a cross-linking agent in quantities of (0; 0.5 and) 1 phr.

Zinc oxide was applied as the activator of ACA in quantities of 4 phr [1]. ZnO powder was manufactured with indirect method by Wiehart, (*Austria*) and has a purity of 99,8% with the density 5.6 g/cm<sup>3</sup> and specific surface area 300 m<sup>2</sup>/g .

## 11.2 Methodology

### 11.2.1 Blending

LDPE and LLDPE polymeric materials in the form of granulates were melt-mixed by a single screw extruder to perform a homogeneous blending. 80; 85 and 90 phr of LDPE matrix was used as a basic material to blend with 20; 15 and 10 phr of LLDPE, which was added to compose chosen ratios. Resultant string was cut after leaving an extruder, to provide a compound of polymer blend, which is more comfortable to handle. From the physical point of view, there were performed a mechanical melt blending at elevated temperature higher than  $T_m$  which have supported a suitable blend production. The velocity of 55 rev/min were applied on a mixing blend. Technology process of blend preparation was carried out at a temperature profile described below in the table (3).

Table (3): Temperature profile of polymer blending.

Zone	Under the hopper	1. Zone	2. Zone	3. zone	Die
Temperature	151 °C	166 °C	181 °C	188 °C	190 °C

### 11.2.2 Mixing

Further mixing of polymer blend granulates with additives (ACA, ZnO, DCP) was established by using a *Brabender W50 EHT*, (*Germany*). Individual components were added consequently and were left for 3 – 5 minutes to assure a sufficient homogenization. Firstly, the polymer granulates were plasticized followed by gradual addition of blowing agent, activator and cross-linker. Mixing was carried out at adequate 30 rev/min and at a temperature 130 °C, which is above a  $T_m$  of polymer but below the  $T_d$  of blowing agent. As the result of mixing procedure was obtained a homogeneously blended mixture of polymer and foaming additives.

### 11.2.3 Foaming

Since LDPE is a crystalline polymer and thus the movement of polymer chains is restricted, a processing temperature should be above the melting point of polymer matrix to ensure a flexibility hence a foaming of polymer [50]. Nevertheless, at increased temperature, the viscosity and the melt strength of polymer decreases dramatically, which may result in a cell wall rupture due to a lack of flexibility. Therefore in this experiment there is used a cross-linker. Moreover, these samples were prepared by chemical foaming with usage of azodicarbonamide and dicumyl peroxide in order to improve their melt strength and thus achieve proper foamability. Final foam structure was prepared by pressing in one step hydraulic press within enhanced temperature, when chemical blowing agent was decomposed in a polymer and N<sub>2</sub> (65%), CO (25%), CO<sub>2</sub> (5%) NH<sub>3</sub> (5%) [41].

One-step compression process of blended compounds was performed by hydraulic press *FONTIJNE LabEcon 300 (The Netherlands)* with facilities to control pressure and temperature. The maximal process temperature is 300 °C and closing force up to 300 kN.

To achieve a sufficient level of diffusion and dissolution of a blowing and a cross-linking agent, the mold pressing was carried out for 20 minutes under the constant pressure force 100 kN kept by automatic hydraulic press. After releasing the force, expansion occurred immediately and homogenously in two directions. Small sheets or plaques, respectively with the size 12x12 cm were obtained as a resulting sample of foamed products, which were cooled at ambient conditions to room temperature.

### 11.2.4 Density

Since obtained foams are mainly closed-cell structures, there was measured a density by hydrostatical method by applying equation (21), where  $\rho_s$  is the density of sample,  $m_a$  and  $m_l$  respectively, is the weight of sample measured within air and liquid.

$$\rho_s = \frac{m_a}{m_a - m_l} \cdot \rho_l \quad (21)$$

This method is suitable for solids of irregular shape and works on Archimedes principle. It is based on weighing a testing specimen in both the air and a liquid of defined



density. Density measurement was performed at room temperature 23 °C and as the liquid was used a demi-water at a room temperature 23 °C which has a density 997,541 kg/m<sup>3</sup>, obtained from a table of physical properties[7].

#### **11.2.5 SEM**

SEM Vega II LMU, (*Czech Republic*) was used to study a morphology of pores at acceleration voltage of 5 kV. Brittle fracture was achieved by breaking sheet samples after rapid cooling in a liquid nitrogen to save clear cellular structure on the surface, usable for SEM imaging. Quantitative image analysis was performed in order to determine a cell size morphology, cell size distribution and a mean cell size of prepared foamed structures.

#### **11.2.6 Thermal conductivity**

Tci thermal conductivity analyzer, C-therm, (*USA*) was employed to determine thermal properties of prepared foams.

Thermal conductivity was measured on treated surface of foamed specimen. The surface was modified by second process step in order to obtain pores directly on the surface; therefore, the structural surface was removed by emery-paper. 500 g load was applied on the specimen during the whole measurement to ensure a good contact between the testing sample and measuring sensor surface. No special measuring medium was used because of porosity structure of the specimen.

Testing sample has thickness of app. 5 mm. The employed setup for thermal conductivity measurement allows to measure materials in the range from 0.01 to 10 W/mK.

#### **11.2.7 DSC**

Thermal properties of foamed samples were studied using Mettler DSC-1 *Mettler Toledo, (Switzerland)*. Measurements were performed under the inert gas atmosphere (N<sub>2</sub>) and the weight of samples were approximately 3.5 mg. Experiments were conducted between -70°C and 160 °C, the temperature mode is listed in a Table (4). First, the samples were heated up to 160 °C and hold for 10 min to erase a thermal history of polymer. Step

of first cooling was driven until -70 °C in a rate of 20°/min and the sample was kept at -70°C for 10 min.

Table (4): Thermal conditions of DSC measurement.

	1 <sup>st</sup> heating	Hold	1 <sup>st</sup> cooling	Hold	2 <sup>nd</sup> heating	2 <sup>nd</sup> cooling
Number	1	2	3	4	5	6
Temperature conditions [°C]	25/160	/	160/-70	/	-70/160	25/-70°C
Rate / Time	20°C/min	10 min	20°C/min	10 min	20°C/min	20°C/min

Melting temperatures, heat enthalpy and crystallinity of polymer matrices and foamed samples were determined from raw data using Star System (Mettler Toledo). Specifically calculation of crystallinity was performed by dividing the measured heat of fusion by the heat of fusion of a 100% crystalline material (293 J/g for polyethylene).

### 11.2.8 DMA

In this study, dynamic mechanical analyzer *DMA 1, Mettler Toledo, (Switzerland)* was employed to measure dynamic mechanical characteristics of prepared foams. DMA 1 allows multipurpose measurements at defined environment in modes of standard deformation including also compression mode usually used for measurement of foams. Temperature range is available from -190 °C up to 600 °C while using a nitrogen atmosphere, frequency range lies between 0.001 and 300 Hz, and the minimal force and the peak force is 0.001 N and 10N as is stated in a Table (5).

Table (5): DMA 1 specifications.

<b>Temperature range</b>	-190 °C – 600 °C
<b>Peak force</b>	10 N
<b>Minimal force</b>	0.001 N
<b>Frequency range</b>	0.001Hz – 300 Hz

First, for each tested sample were linear viscoelastic region by applying of different displacement while measuring the response of dynamic stimulation. Viscoelastic behavior of foamed polyolefins was determined within a frequency mode of dynamic mechanical compressing. To complete all data describing a foam behavior in a compression there was performed a measurement in the broad temperature range. The conditions for individual measurements are listed in the Table (6). All experiments were performed on the samples of cylindrical shape with the diameter 10 mm and the thickness ranging between 5.1 – 5.3 mm.

Table (6): DMA measurement method.

Mode	Temperature [°C]	Frequency/range [Hz]	Displacement [μm]	Load [N]
Linear(1)	25	1	0.1 - 100	2
Frequency	25	0.1 - 10	20	2
Temperature	-150 to 110	0.5 ; 1; 2.5; 5		2

## 12 RESULTS AND DISCUSSION

Performed investigations of chosen properties of prepared foams with respect to chemical structure of used PEs have showed that foamed materials studied in this thesis exhibit the changes corresponding to the presence of the gas-filled pores and thus influencing the final properties. Further aspect influencing the final properties is ratio between the LDPE and LLDPE, which was mainly under consideration in this thesis.

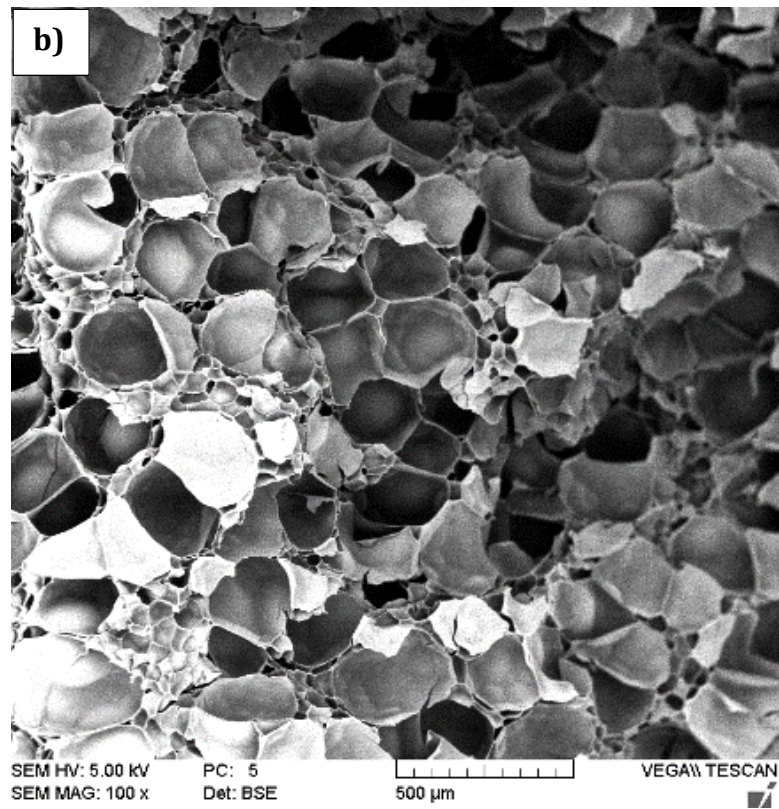
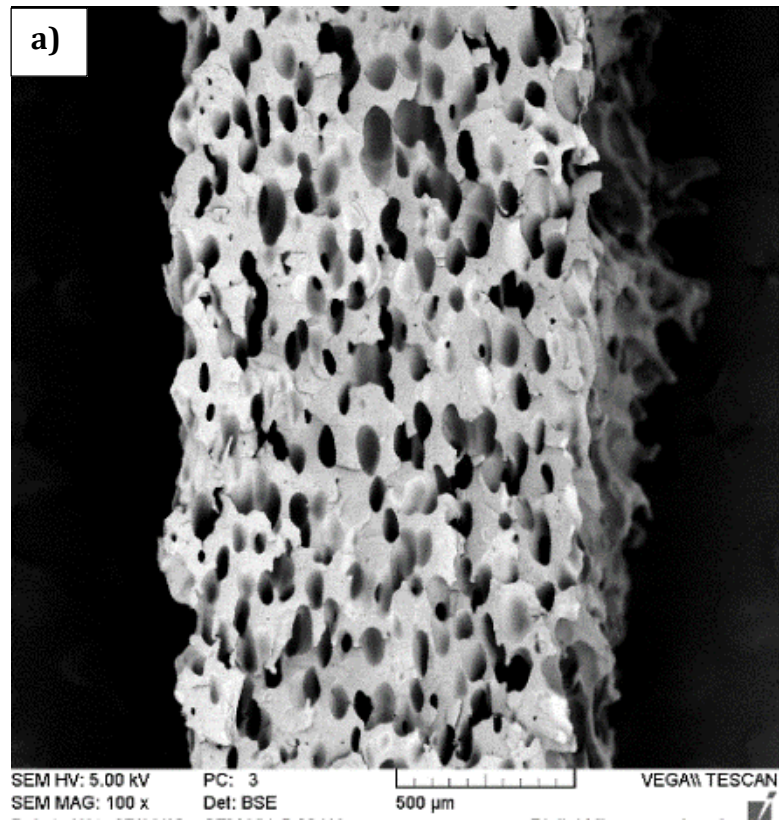
### 12.1 Density

A relative density for various types of foams in Table (7) was calculated according to the equation (21). Density is one of the most important characteristic of two-phase material (foams).

Table (7): Relative densities of samples.

<b>Sample</b>	<b>Ratio</b>	<b>Relative density [kg/m<sup>3</sup>]</b>
<b>LDPE/C4-1</b>	90/10	114,47
	85/15	88,91
	80/20	93,54
<b>LDPE/C4-2</b>	90/10	102,5
	85/15	84,82
	80/20	99,90
<b>LDPE/C8-1</b>	90/10	78,39
	85/15	91,35
	80/20	95,10
<b>LDPE/C8-2</b>	90/10	84,71
	85/15	74,20
	80/20	80,45

## 12.2 SEM



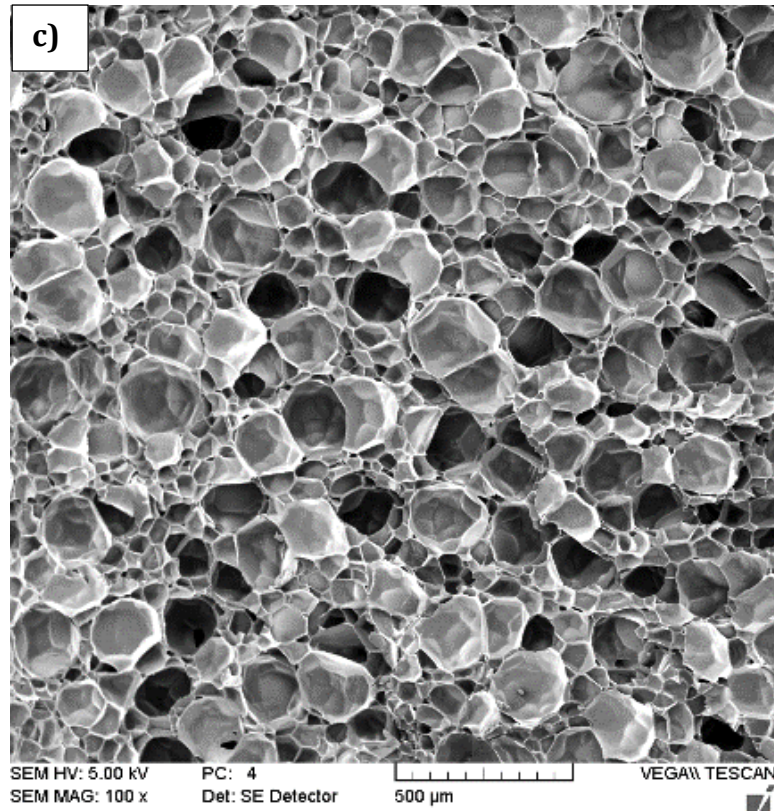
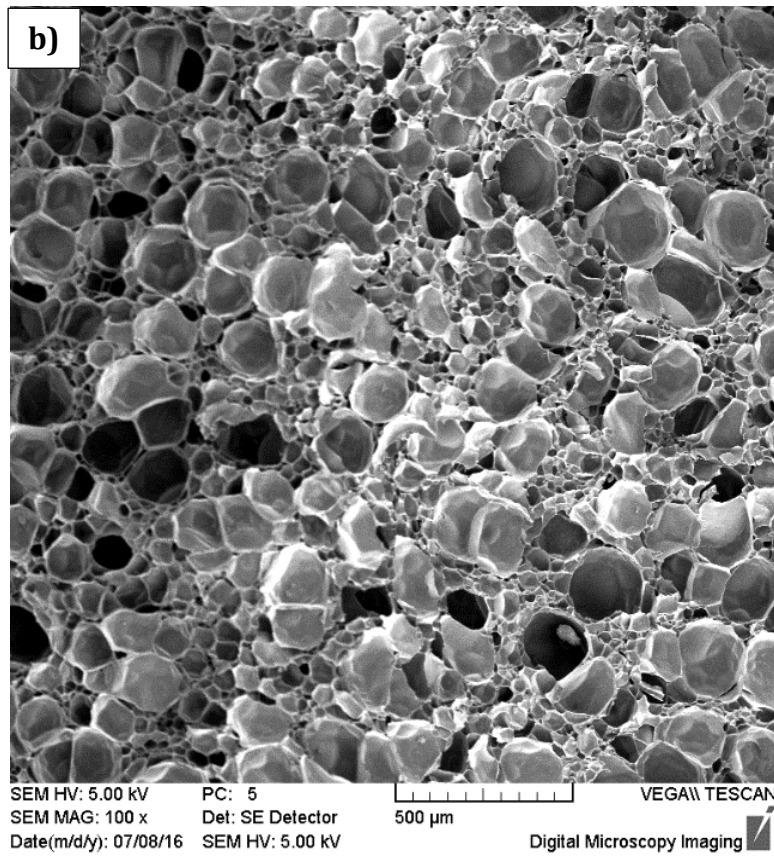
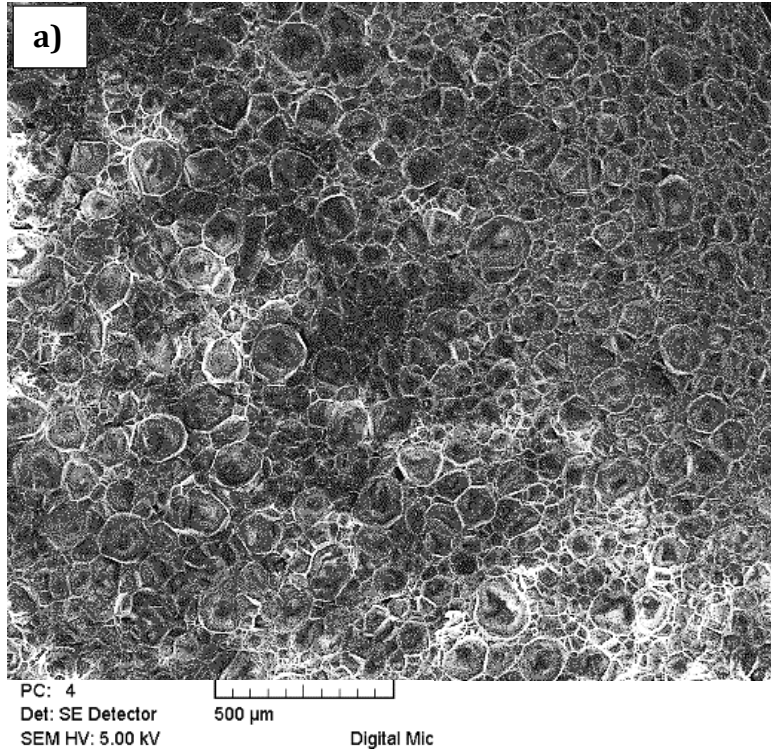


Figure (18) SEM images of the foams containing a) 0 phr; (b) 0,5 phr; (c) 1 phr of cross-linker with magnification 100x.

SEM images in the Figure (18) show optimization of cellular structure by varying a cross-linker content. With no addition of cross-linking agent there was obtained such a low-foamed structure with even incomplete pores. It is obvious that at least 1 phr of cross-linker Figure18 (b) is needed to perform a desired fine cellular structure.



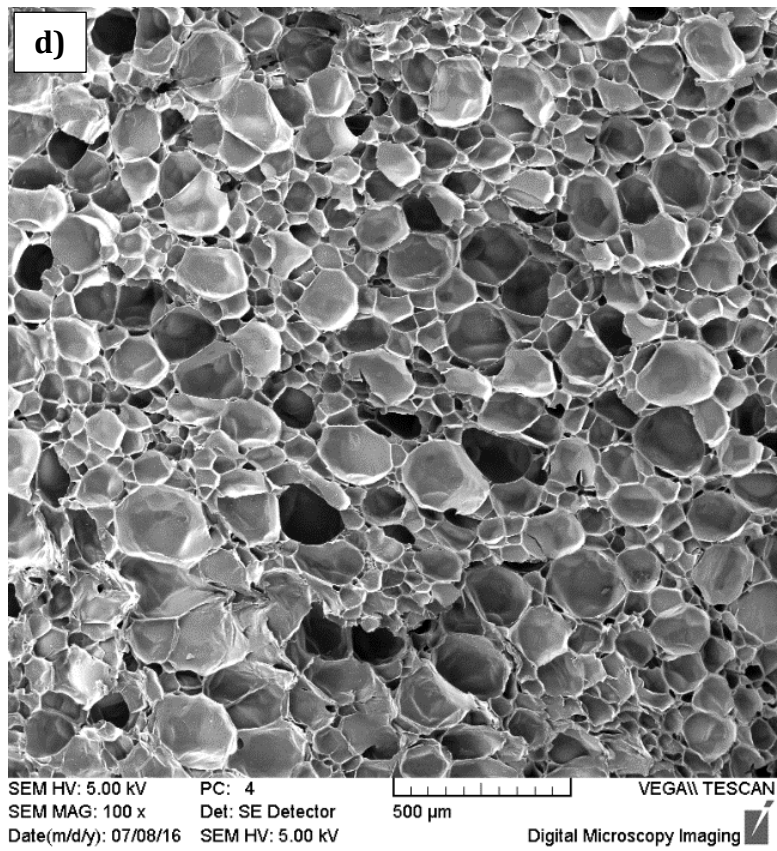
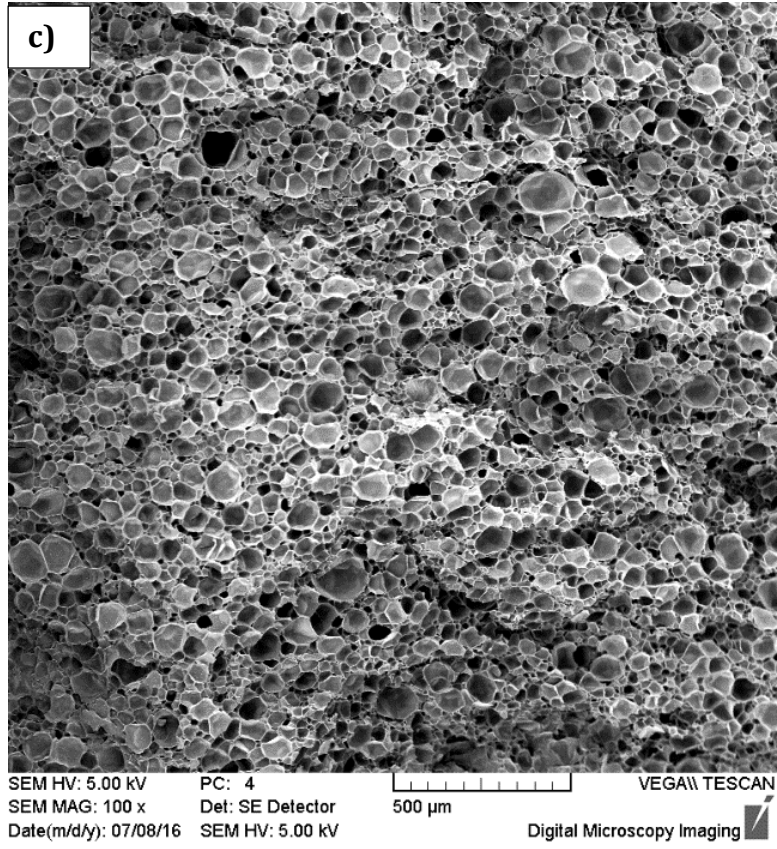




Figure (19): SEM micrographs displaying a) LDPE matrix; and LDPE/LLDPE blends of ratios b) 90/10; c) 85/15; d) 80/20; with magnification 100x.

Typical cellular structure of foamed LDPE is presented in the Figure (19). Obtained cellular structures vary in several parameters with respect to application of different LDPE/LLDPE. As can be seen in graphical representation of measurement in the Figure (19) confirming the numerical results stated in the table (8) there are significant differences between investigated samples. Addition of 15 phr of LLDPE (c) creates the finest cellular structure with the highest number of the smallest pores. Pure LDPE matrix a) and the addition of b) 10 phr and d) 20 phr of LLDPE behave similarly.

Table (8): Number of pores contained in investigated samples.

<b>Sample</b>	<b>Ratio</b>	<b>Number of pores / mm<sup>2</sup></b>
<b>LDPE</b>	-	191
<b>LDPE/C4-1</b>	90/10	249
	85/15	264
	80/20	441
<b>LDPE/C4-2</b>	90/10	238
	85/15	825
	80/20	134
<b>LDPE/C8-1</b>	90/10	296
	85/15	321
	80/20	138
<b>LDPE/C8-2</b>	90/10	210
	85/15	433
	80/20	328

### 12.3 Thermal Conductivity

Thermal conductivity was investigated in order to prove insulating properties of prepared foams with respect to their final application in thermal insulations. Figure (20) shows experimental results, which are presented in table (9).

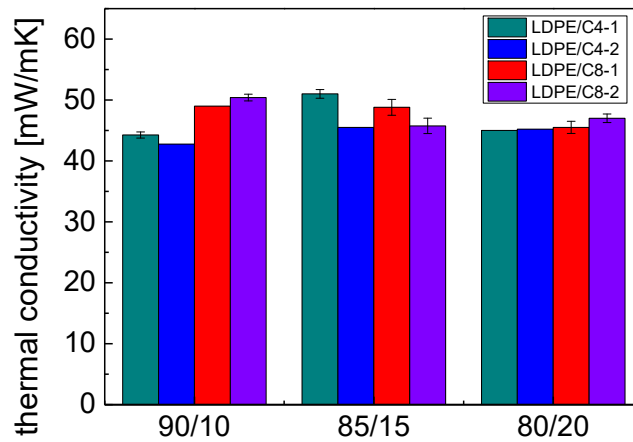


Figure (20): Thermal conductivity of tested samples grouped in according to LDPE to LLDPE ratio.

Obtained data describe thermal conductivity [mW/mK] of tested samples. There are no significant differences between compared samples. Thermal conductivity of prepared PE foams vary between 43 mW/mK for LDPE/C4-2 in ratio 90/10 which can be caused by presence of lower amount of bigger cells therefore higher amount of trapped air inside, and 51 mW/mK for sample LDPE/C4-1 in ratio 85/15 with fine cellular structure.

When compared to competitive materials such as PU foams which are characterized by thermal conductivity around 35 mW/mK [51].

Table (9): Numerical results of thermal conductivity [W/mK] of tested samples.

Sample	Ratio	Thermal conductivity [mW/mK]
LDPE/C4-1	90/10	44
LDPE/C4-2	90/10	43
LDPE/C8-1	90/10	49
LDPE/C8-2	90/10	50
LDPE/C4-1	85/15	51
LDPE/C4-2	85/15	45
LDPE/C8-1	85/15	49
LDPE/C8-2	85/15	46
LDPE/C4-1	80/20	45
LDPE/C4-2	80/20	45
LDPE/C8-1	80/20	45
LDPE/C8-2	80/20	47

<b>LDPE/C4-1</b>	90/10	44
	85/15	51
	80/20	45
<b>LDPE/C4-2</b>	90/10	43
	85/15	46
	80/20	45
<b>LDPE/C8-1</b>	90/10	49
	85/15	49
	80/20	46
<b>LDPE/C8-2</b>	90/10	50
	85/15	46
	80/20	47

## 12.4 DSC

For relevant comparison there were tested also granules of each raw substance before its blending. Foams were prepared from LDPE blended with LLDPE which are both characterized by glass transition region started from -130 °C to 100 °C and melting region from 100 °C to 115 °C for LDPE and from 122 °C to 127 °C for LLDPE, respectively.

In order to confirm the difference in the DSC characteristics of foamed samples there were also tested sample in form of granule as can be seen in Figure (21) showing the shift of melting temperature as well as crystallization temperature to lower temperatures. This slight shift of melting temperature from 113.6 °C to 109.4 °C and small change of heat fusion from 115,6 J/g to 123,3 J/g can be caused by processing technologies applied on raw material (slight degradation of materials can be achieved) as well as due to the presence of additives (cross-linker and activator). Such change can be attributed to the decreased molecular weight of LDPE or LLDPE foams in comparison to virgin material probably due to the processing conditions (compounding, compression molding).

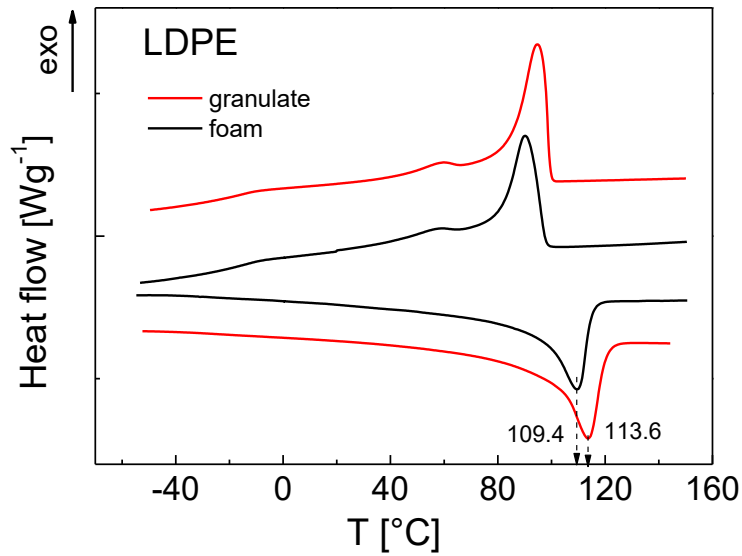


Figure (21): Second heating thermal scan of DSC analysis of granulated and foamed LDPE matrix.

As can be seen in the Figure (21) *LLDPEs* used in this study varying in the length of the side chain C4 or C8 where number corresponding to the amount of carbons in that side chain. Experimentally obtained values of melting temperature, showing differences from the highest 123.5 °C for C4-1 sample to 72.6 °C for C8-2 specimen. Such behavior was further observed for the blended foams where such characteristic temperatures are between the temperatures of individual component (LDPE, LLDPE).

A typical DSC curve for the LDPE samples can be seen in the Figure (22) while the numerical results of obtained melting points and crystallization points as well as an enthalpy and crystallinity of foams under study are listed in the Tables (10,11). Within a graphical evaluation, the melting point was taken as a minimum at the peak of heat flow curve, and Y axis is individual for each curve, therefore arbitrary values have been used.

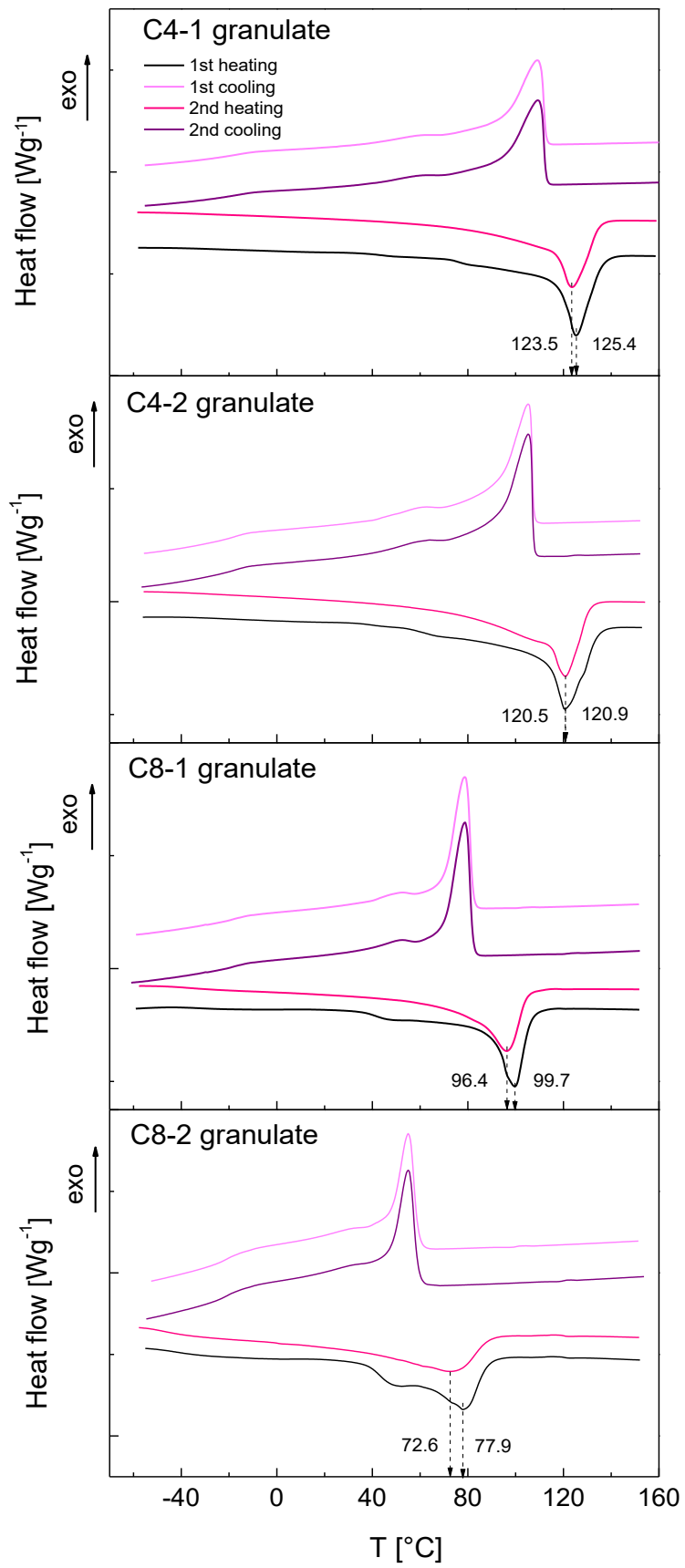


Figure (22): DSC curves of particular virgin LLDPEs and their  $T_m$ .

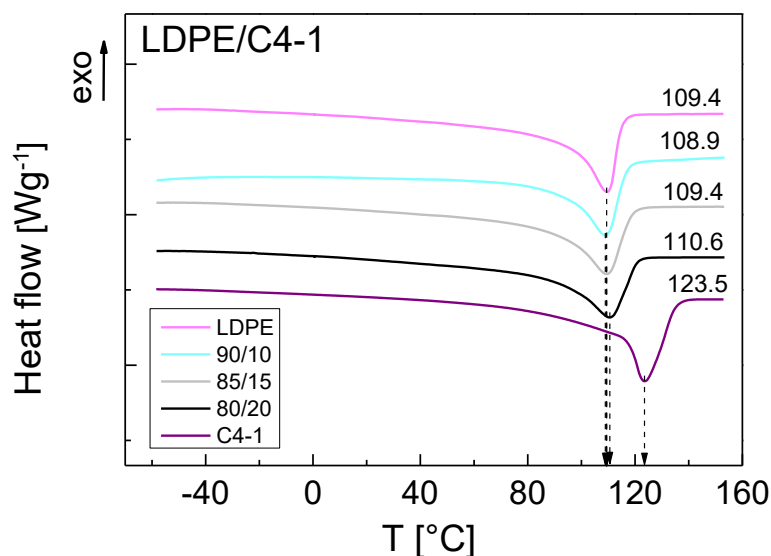


Figure (23): Comparison of *DSC* curves with respect to different component ratio.

Figure (23) shows the thermal behavior and melting points of foamed LDPE matrix and *LLDPE* C4-1 sample with comparison to different ratios of *LLDPE/C4-1* blends. The level of LDPE is 90 phr, 85 phr and 80 phr. It is obvious, that the higher LDPE to LLDPE ratio corresponding to low addition of LLDPE with defined chemical structure and behave rather similar to the matrix in the term of similar melting temperatures.

As can be seen in the Table (10) the amount of LLDPE influencing the thermal properties, namely peak of the melting temperature is highest for samples 85/15 similarly to heat of fusion, indicating that pore distribution and size of the pores play a crucial role. In this case the enhancement is connected to the small pore size and narrow pore distribution.

Table (10): Numerical results from thermal analysis performed by DSC in first heating scan.

1 <sup>st</sup> heating scan		T <sub>m1</sub> [°C] Heating		Heat of fusion [J/g]
Sample		Drop	peak	
LDPE foam	-	51,9	106,8	111,5
LDPE granulate	-	63,0	115,0	118,7
C4-1	-	50,4	80,1	125,4
LDPE/C4-1	80/20	50,1	108,6	95,2
	85/15	54,5	107,7	114,5
	90/10	51,3	107,6	114,2
C4-2	-	45,3	69,0	120,5
LDPE/C4-2	80/20	50,3	107,8	108,9
	85/15	53,0	108,5	120,6
	90/10	37,3	107,0	112,1
C8-1	-	49,7	99,7	84,1
LDPE/C8-1	80/20	49,7	107,2	116,9
	85/15	48,4	105,4	103,2
	90/10	50,4	106,3	100,6
C8-2	-	52,4	77,9	59,5
LDPE/C8-2	80/20	50,7	105,2	91,5
	85/15	50,0	106,8	109,3
	90/10	50,7	105,2	106,8
		52,4		

In case of the second DSC scan the results are slightly shifted Table (11), however follow the trend from first scan. In case of cooling the crystallinity was calculated and it can be stated generally that foams containing C4 LLDPEs exhibit higher crystallinity in comparison to the C8 LLDPEs. Other parameters such as amount of the individual components do not significantly affected other DSC results. The role of the crystallinity on the mechanical properties of the fabricated foams will be discussed in the following chapter.

Table (11): Numerical results from thermal analyses performed by DSC in first cooling and second heating scan.

1 <sup>st</sup> cooling scan 2 <sup>nd</sup> heating scan		T <sub>m2</sub> [°C] Heating	Heat of fusion [J/g]	T <sub>c</sub> [°C] Cooling	Crystallinity [%]
Sample					
LDPE foam	-	109,4	115,6	90,3	39,2
LDPE granulate	-	113,6	123,3	94,6	41,8
C4-1	-	123,5	119,3	109,0	40,7
LDPE/C4-1	80/20	110,6	122,3	93,8	41,6
	85/15	109,4	129,3	93,4	44,1
	90/10	108,9	121,0	94,2	41,1
C4-2	-	120,9	120,5	105,1	41,0
LDPE/C4-2	80/20	109,4	113,0	93,3	38,7
	85/15	108,9	126,0	92,9	42,9
	90/10	110,7	112,1	91,1	42,0
C8-1	-	96,4	94,6	78,6	32,0
LCPE/C8-1	80/20	106,5	121,0	91,3	41,3
	85/15	106,4	106,9	91,4	36,3
	90/10	106,6	108,2	92,9	36,5
C8-2	-	72,6	58,0	55,0	19,3
LDPE/C8-2	80/20	107,5	106,6	88,3	36,1
	85/15	107,1	119,3	91,3	40,1
	90/10	105,5	116,8	92,9	39,0

## 12.5 DMA

Parallel-plate geometry was used for measurement and further investigation of the dynamic mechanical properties in the linear viscoelastic region. The values of storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss tangent ( $\tan \delta$ ) were extracted from the all



measured variables as representative ones for describing. The mechanical properties can be described by plastic deformation in the cell walls, which occurs during the cyclical deformation under certain stress application.

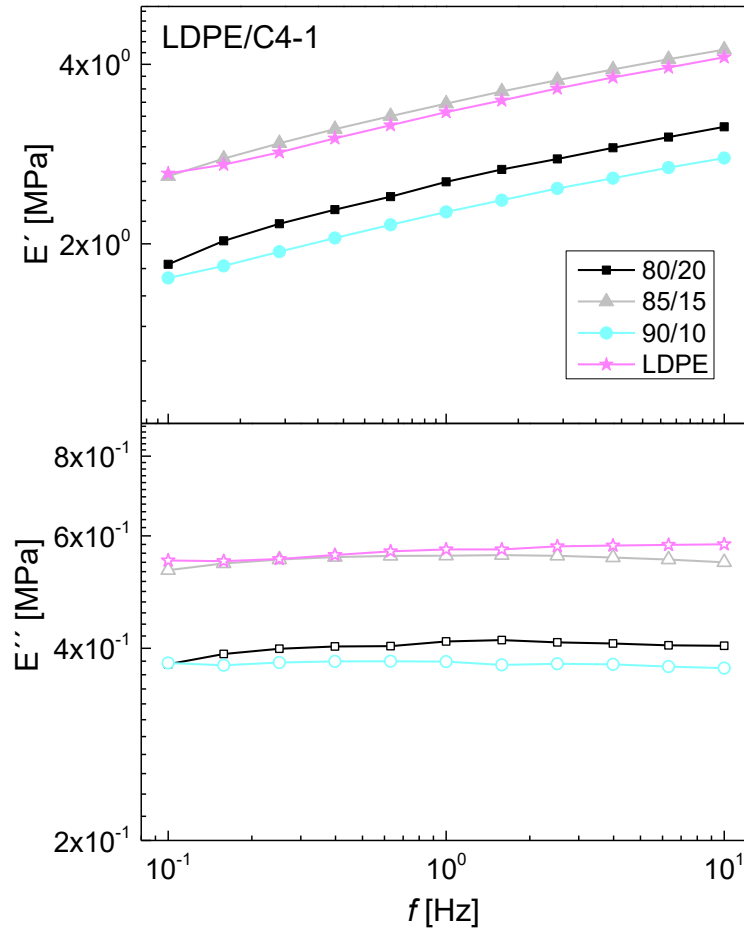


Figure (24): Frequency dependence of the storage and loss moduli for LDPE/C4-1 foam.

Figure (24) shows the highest storage and loss moduli for ratio 85/15 for sample LDPE/C4-1, which is almost equivalent to LDPE matrix. Rather lower moduli were obtained with less suitable cellular structure in the ratio of 80/20 and 90/10 respectively.

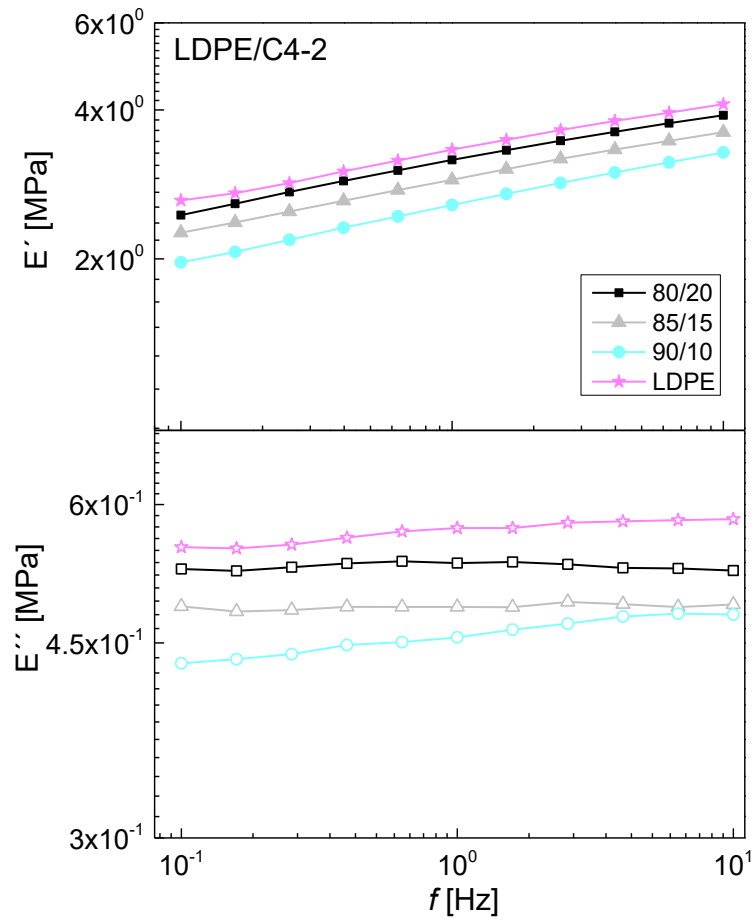


Figure (25): Frequency dependence of the storage and loss moduli for LDPE/C4-2 foam.

Figure (25) describes frequency dependence of the storage and loss moduli for sample LDPE/C4-2, where the similar results to LDPE were obtained in the ratio 80/20, but again there are no very significant differences.

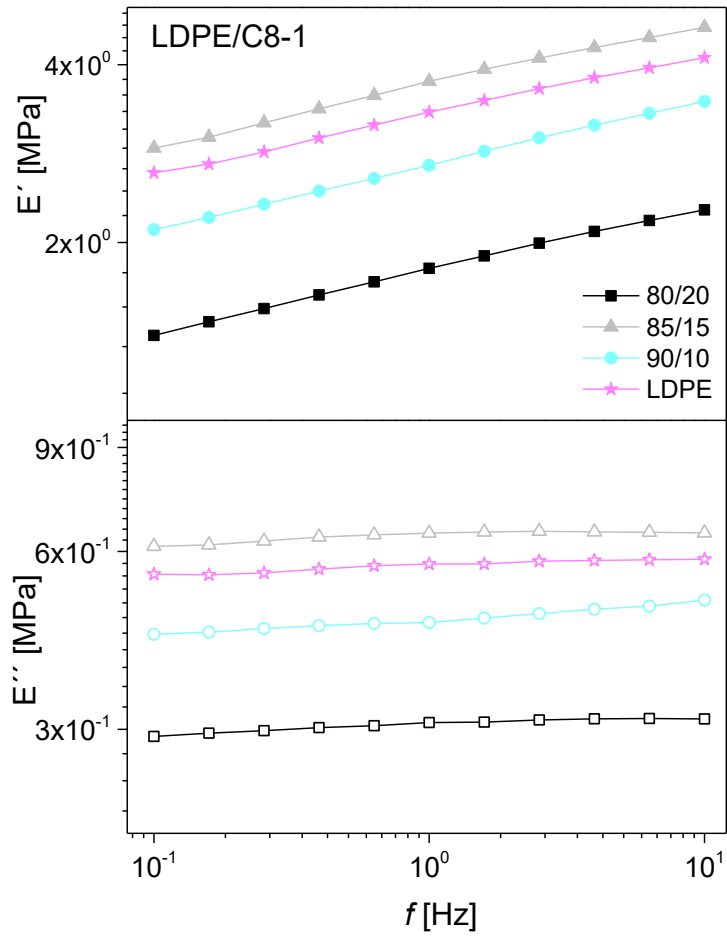


Figure (26): Frequency dependence of the storage and loss moduli for LDPE/C8-1 foam.

Figure (26) shows the highest mechanical properties of 85/15 ratio for sample LDPE/C8-1, when investigating storage and loss moduli as frequency dependent.

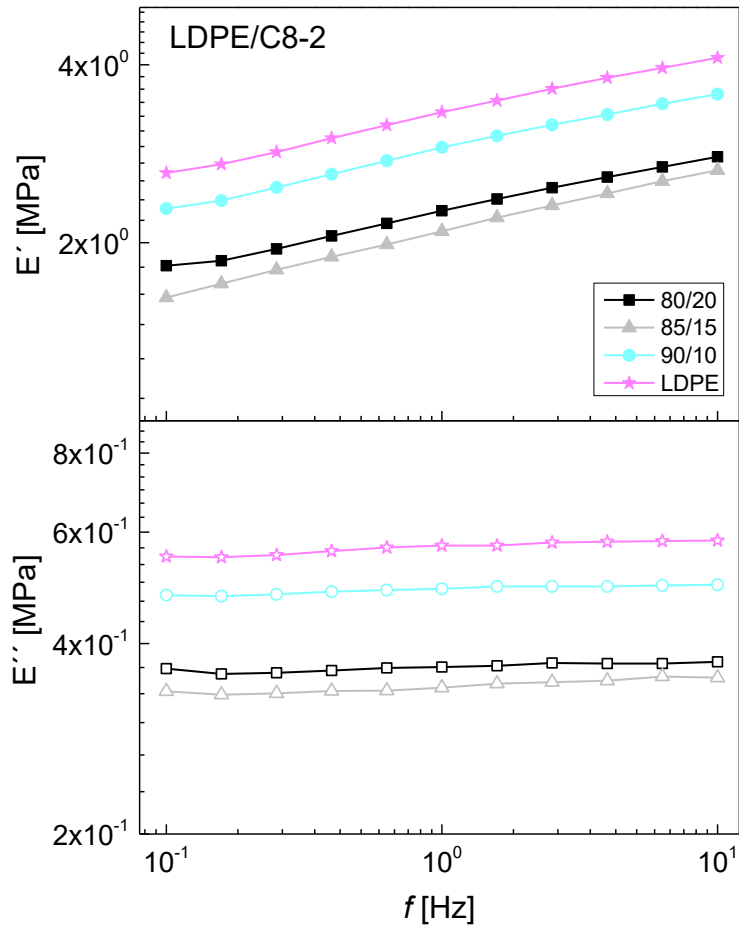


Figure (27): Frequency dependence of the storage and loss moduli for LDPE/C8-2 foam.

Figure (27) shows obtained storage and loss moduli of the sample LDPE/C8-2, where the comparable and almost equal results can be seen with the ratio 90/10 and thus the lower addition of LLDPE in a matrix LDPE.

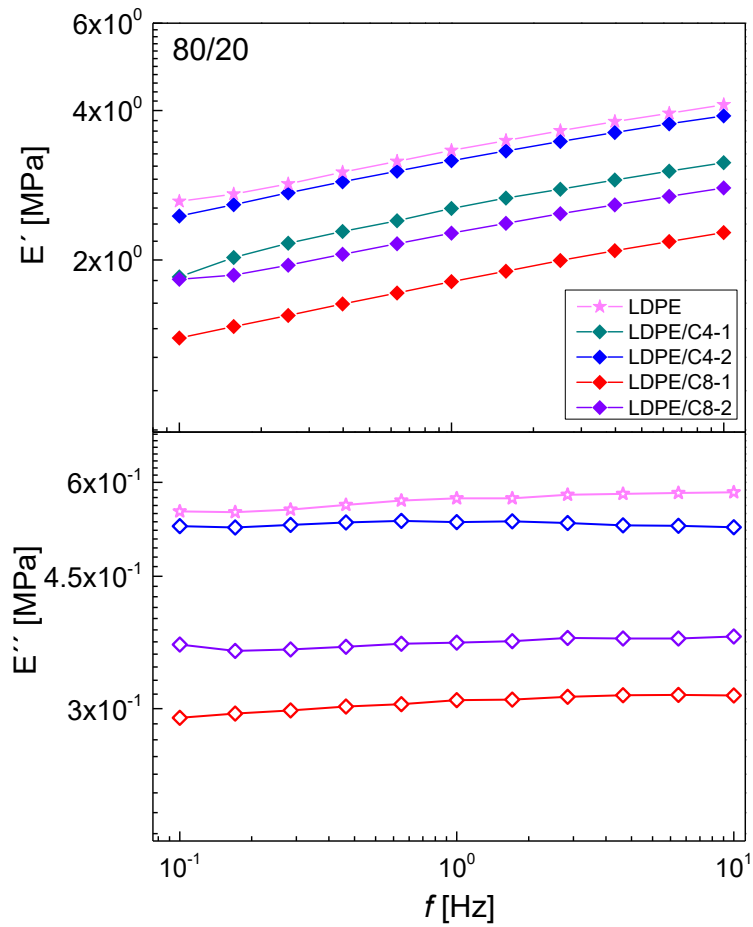


Figure (28): Frequency dependence of the storage and loss moduli for various LDPE to LLDPE ratios.

Figure (28) shows the highest loss and storage modulus with the sample of LDPE matrix when compare to LDPE/LLDPE blend in ratio 85/15. On the contrary, the lowest mechanical properties described by dynamic mechanical analysis belong to LDPE/C8-1-80/20 accompanying by the lowest crystallinity of compared 80/20 ratio samples.

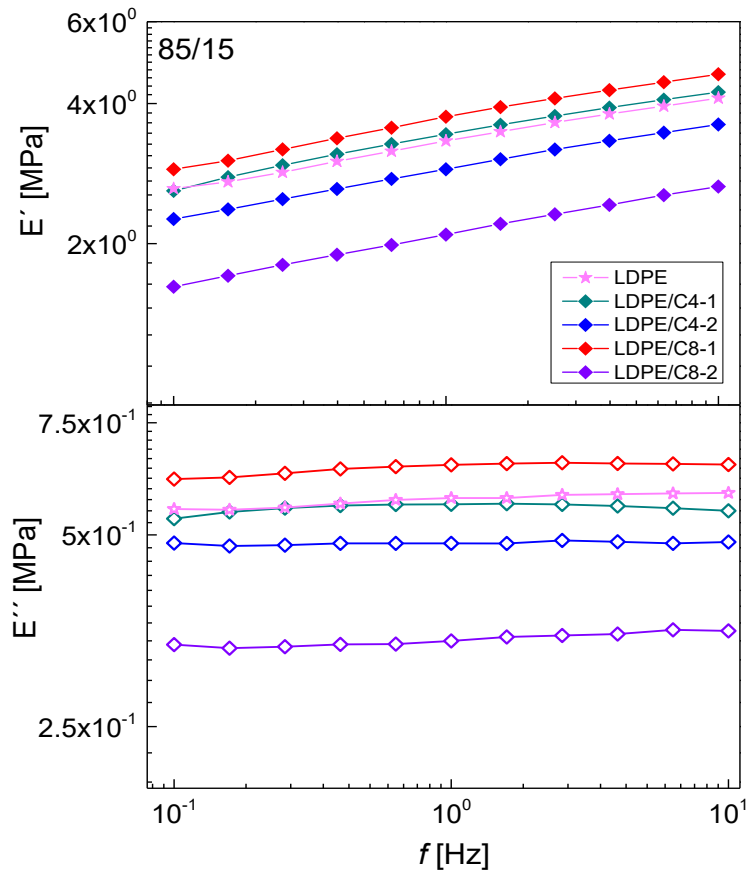


Figure (29): Frequency dependence of the storage and loss moduli for various LDPE to LLDPE ratios.

As can be seen in the Figure (29) there is a slight dependency on the applied frequency during measurement indicating the cross-linked nature of the fabricated foams. The highest storage modulus was obtained for sample LDPE/C8-1-85/15. The main reason is well developed porous structure as could be observed from SEM images. The enhanced crystallinity also contribute to the improved storage modulus as was confirmed on the sample LDPE/C4-1-85/15 which served similar behavior to the neat LDPE foam. The loss modulus which can be classified as a capability of material to absorb the mechanical energy and transform it to heat, was found to be best for sample LDPE/C8-1-85/15, which can be utilized in various damping applications. Other fabricated foams exhibit similar or worse mechanical performance in direct comparison the neat matrix.

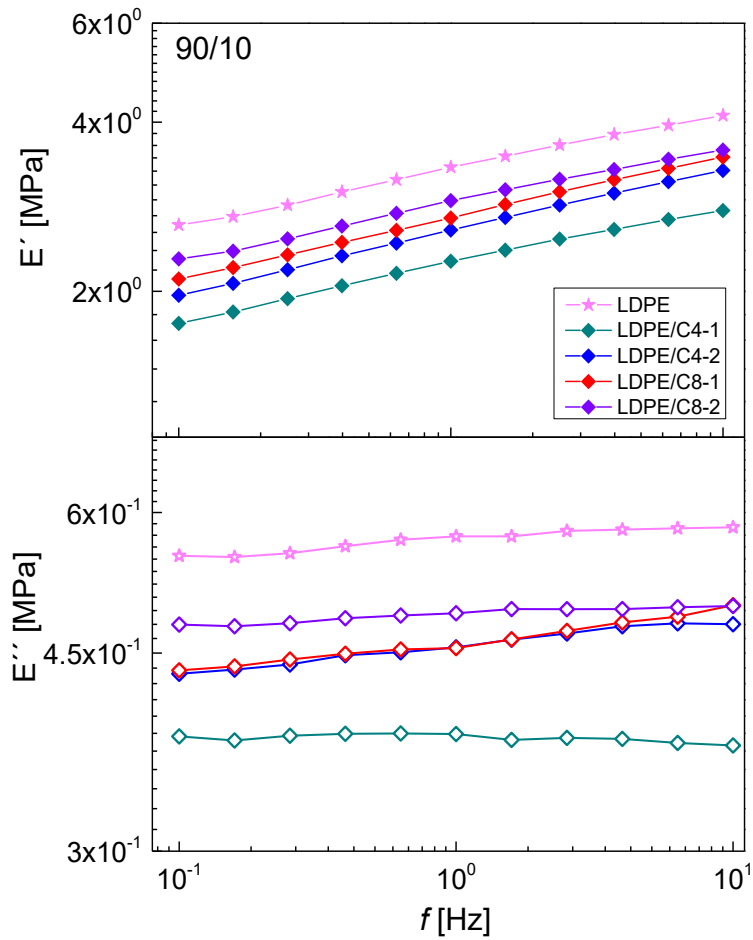


Figure (30): Frequency dependence of the storage and loss moduli for various LDPE to LLDPE ratios.

In case of other compositions namely 80/20 and 90/10, due the fact that pores were not properly developed (the size and pore distribution), they are too big and distribution is wide, the mechanical performance of neat LDPE foam was higher. In this case the effect of the crystallinity, was not good enough to provide system with improved mechanical properties.

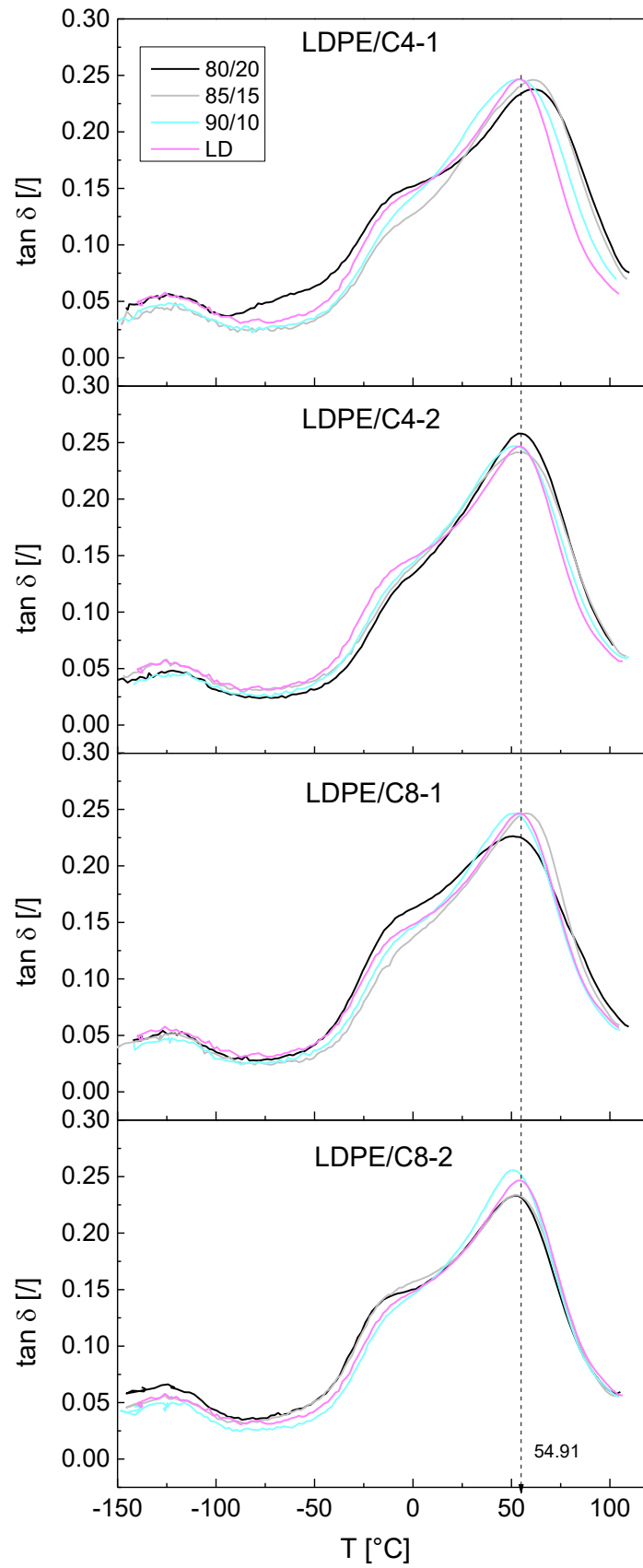


Figure (31): Temperature dependence of the  $\tan \delta$  for various LDPE-based foams.



As can be seen from the Figure (31) the dependence of the  $\tan \delta$  on the temperature can provide the information about characteristic phase transitions. The peak corresponding to approximately  $-125\text{ }^{\circ}\text{C}$  can be assigned to the  $T_g$  of the LDPE and also LLDPE, the fact is that the  $T_g$  is rather similar for both of these components. The significant peak can be seen at app.  $50\text{ }^{\circ}\text{C}$  corresponding to the melting of the crystalline phase of side chains. The presence of the crystalline structures at this region was also reported by Janicek et al [52]. The shoulder at  $25\text{ }^{\circ}\text{C}$  can be probably attributed to the short polymer chains present in the foams as a result of degradation during processing. In this case, polymer chain shorter than side chains of the LDPE and LLDPE. The positions of the peaks corresponding to the  $T_g$  are shifted only slightly, however more significant change can be seen in case of melting peak, where the composition as well as crystallinity can play important role.

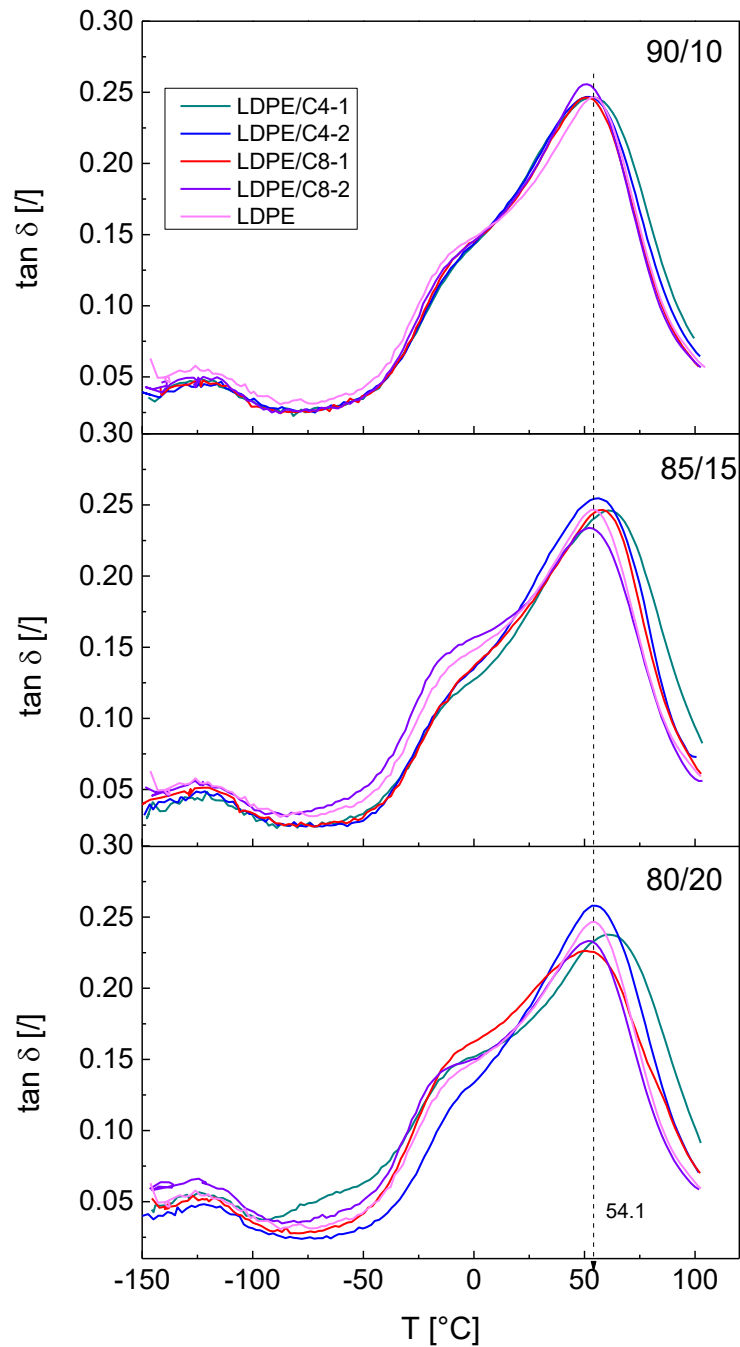


Figure (32): Temperature dependence of  $\tan \delta$  for various LDPE to LLDP ratios.

Phase transitions corresponding to presented measurements were already described above. The Figure (34) shows comparison of temperature dependence of  $\tan \delta$  for different LDPE to LLDP ratios. LDPE/C4-1 behave more significant shifts in  $T_g$  and other peaks corresponding to already mentioned phase transitions.

In order to evaluate the mechanical performance of the fabricated foams, the storage modulus was investigated in the broad temperature range from -150°C to 100°C (Figure 33), representing the application window of the foams. In many cases the neat LDPE foam provide stable mechanical performance in comparison to the different analogues. However, and in fact similarly to the frequency dependence the sample LDPE/C8-1 and LDPE/C4-2 at composition 85/15 and 90/10, respectively exhibit improved mechanical performance in comparison to the neat LDPE foam in first case due to the proper structural properties and in second case due to the higher crystallinity.

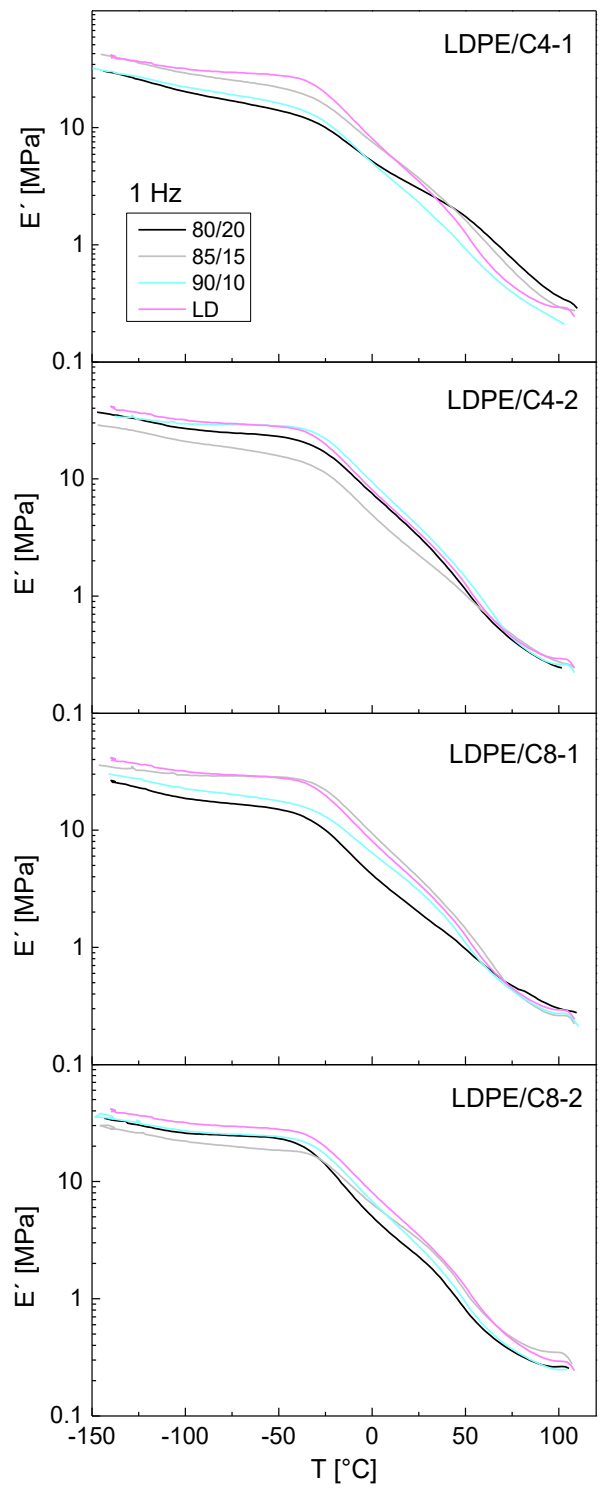


Figure (33): Temperature dependence of the storage modulus for various LLDPE-based foams.

Generally, the measured curves Figure (33) provide typical shape corresponding to various phase transitions such as glass transition or melting transition. Since the LDPE as

well as LLDPE both are above the  $T_g$ , the mechanical properties should be affected by other transitions such as melting of short polymer chains etc. The measurement above the  $T_m$  of individual components also does not make a sense, because even if the material is cross-linked, the gas entrapped in the pores will escape due to enhanced permeability of the material during melting.

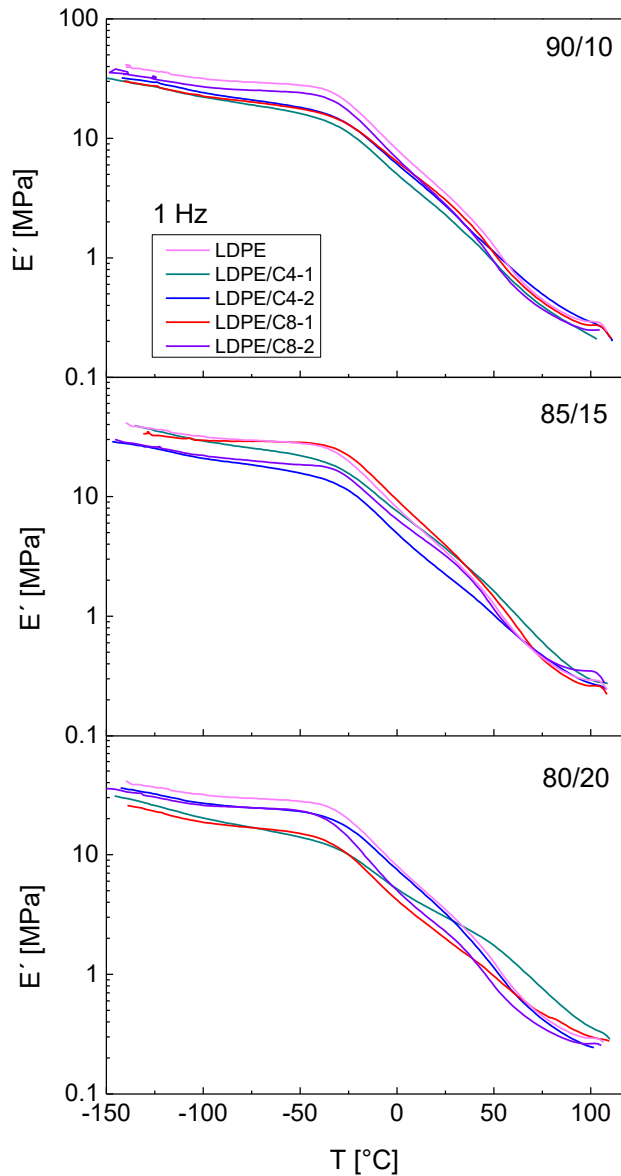


Figure (34): Temperature dependence of the storage modulus for various types of foams.

The Figure (34) describes the mechanical properties with respect to different LDPE to LLDPE ratio. As it was discussed above, different content of LLDPE influences mechanical

properties. In the case of 85/15 ratio, the highest mechanical properties are achieved in the sample LDPE/C8-1 which are very similar or even better than LDPE matrix.

## 13 CONCLUSION

This master thesis was focused on the fabrication of various foam materials and investigation of the effect of the foam composition on the final structural and physical properties. Different types of linear low-density polyethylene (LLDPE) in various ratios (90/10, 85/15, 80/20) to LDPE were used to prepare foamed structures. Utilized LLDPEs were varied in the length of the side chains and chemical foaming was employed in order to achieve the suitable foam samples. SEM investigation proved that composition of the foams strongly affects the size of the pores as well as the pore size distribution. The best structural properties (small pore size and narrow pore size distribution) were obtained for samples with ratio between LDPE and LLDPE 85/15.

The structural properties of foams have significant effect on the characteristic thermal properties investigated by using DSC. In this case, the peak of the melt temperature was found to be highest for samples 85/15 similarly to the heat of fusion. Unfortunately, the composition of the foams does not have the significant effect on the final crystallinity. In this case the nature of the LLDPE (length of the side chains C4 or C8) has significant influence and it was found that crystallinity of the foams is higher for the foams with C4 types of LLDPE, which is in good agreement with theory of crystallinity in LDPE-type of materials.

Thermal conductivity as a crucial parameter for further application of such foam was negligibly affected by nature of the LLDPE as well as the composition. Here can be stated that values of the thermal conductivity are very similar to those obtained for neat LDPE foam and therefore all prepared foams have potential to be used at various thermal insulating applications.

Dynamic mechanical analysis of the fabricated foams proved, that enhanced crystallinity in case of sample LDPE/C4-1 provides the systems with slightly enhanced mechanical properties than neat LDPE. Moreover, it was also found that composition in case of sample LDPE/C8-2 play a crucial role, due to the fact that optimal mechanical performance was obtained for sample 85/15, while the rest of them (90/10 and 80/20)

were significantly suppressed. Such behavior was clearly seen in the of both, frequency and temperature dependence.

Finally, can be stated that utilization of LLDPEs in composition of solid phase in the polymer foams offer the possible tunability of the structural and thermal properties, those can significantly influence the mechanical performance of the final foams when the optimal composition or crystallinity is achieved, while the thermal insulation capabilities were sustained on the same level.



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## LIST OF ABBREVIATIONS

ACA	Azodicarbonamide
BA	Blowing agent
CBA	Chemical Blowing agent
CO <sub>2</sub>	Carbon dioxide
DCP	Dicumylperoxide
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
E'	Storage modulus
E''	Loss modulus
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
PBA	Physical blowing agent
PE	Polyethylene
PET	Polyethyleneglykol terephtalate
PLA	Poly lactide acid
PP	Polypropylene
phr	Per hundreds of resin
PS	Polystyrene
PU	Polyurethane
SEM	Scanning electron microscopy
Tan $\delta$	Loss tangent

$T_d$	Decomposition temperature
$T_f$	Foaming temperature
$T_g$	Glass transition temperature
$T_m$	Melting temperature
WWII	Second world war
ZnO	Zinc oxide
XPE	Cross-linked polyethylene



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