Creation of Microstructered Polymers with Defined Micro and Nano Pores for Different Applications using Hot Embossing and CO_2

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ABSTRACT

Porous polymer materials are essential for a broad range of applications such as automobile parts, medical implants, filtration systems, and catalytic reactors due to a combination of their durability, low weight and cost, and high inner surface. For various of these applications, it is favorable to manufacture microstructures with pores in the range from micrometers to nanometers, also with defined gradients.

In a novel approach, two hitherto separately applied methods, namely hot embossing for microstructuring of polymers and saturation with CO_2 under pressure at different temperatures and exposure times are now combined: (i) In a first step, a polymer is microstructured by hot embossing. (ii) In a second step, these microstructures are exposed to CO_2 for the pore production. Afterwards they are thermally treated also at different temperatures for different durations.

By the combination of these two methods, with a so far completely different application spectrum, the original material properties of the polymers are modified. Microstructured materials with interconnected pores can be fabricated, but also pore gradients from micro to nano size exhibiting improved mechanical and physico-chemical properties. With this method, even the viscoelastic properties of thermoplastic polymers can be tuned by adjusting smoothly graded micro to nano-structures inspired by structural hierarchies and the related excellent mechanical properties of biological materials. Also ultra-thin porous poly-methyl-methacrylate (PMMA) films exhibiting a bright white color, as known from the white beetle of the genus *Cyphochilus*, can be produced by this saturation method using CO_2.

INTRODUCTION

Materials with porous structures have a big impact on scientific and industrial questions in completely different subjects, e.g. materials sciences, separation processes as filtration and adsorption or catalysis for chemical reactions. The potential industrial applications reach from automobile suppliers and medical implants or medications to filter and adsorbent materials or catalysts for chemical reactions. In all these fields, many structures need to consist of pores of micro or nano size, sometimes in thin membranes, or with defined pore gradients, so-called hierarchical pores, in order to improve and to fine-tune the properties of materials: (i) for separation purposes, bigger effective surfaces or a higher surface-volume-ration are needed (often in membranes), which can be achieved by porous materials [1], (ii) for catalysts a well-accessible high inner surface and an enhanced fixation of catalytically active substances is desired for an improved efficiency by nano structures, which can also be achieved by pores [2], (iii) for improved stiffness of materials, hierarchical pore structures may be a solution, inspired by nature like adhesive structures of geckos, ladybird beetle legs or visco-elasticity in pomelo peel [3], (iv) for optical properties ultra-thin porous films, inspired by the white beetle of the genus *Cyphochilus* to produce white surfaces [4].

MATERIALS AND METHODS

In a novel approach, two hitherto separately applied methods, namely hot embossing (or as a variation of it the so-called pull drawing) for microstructuring of polymers and saturation with CO_2 under pressure to produce porous structures are now combined, as shown in Figure 1.

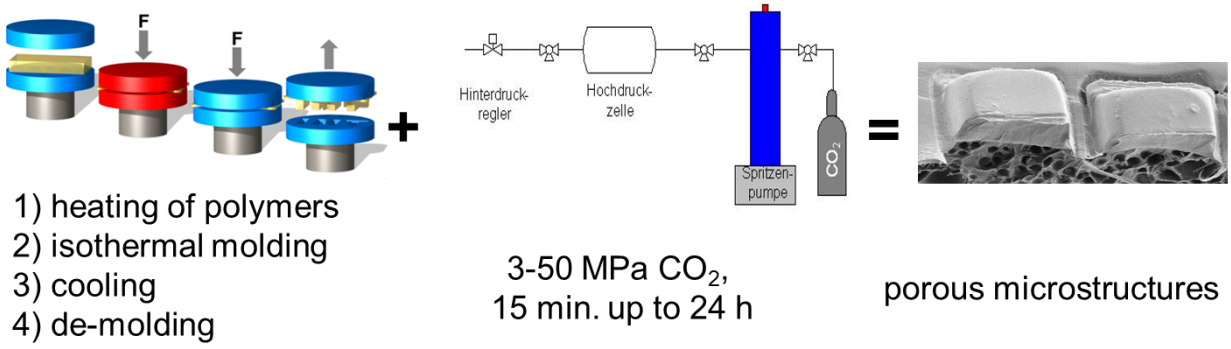

Figure 1. Schematic of combined processes for hot embossing and CO_2 saturation for production of porous structures

In a first step, a polymer material is microstructured by hot embossing in four stages, namely the polymer is heated, micro- or nanostructured by isothermal molding, cooled and de-molded. Micro and nano structures (as shown in Figure 2) can be produced. The range of products lasts from hot embossing for the fabrication of hierarchical microstructures in polymers (Fig. 2A) over nanostructured columns of 140 nm diameter a high aspect ratio of 1:10 (Fig. 2B) to super hydrophobic “nanofur” surfaces produced by hot pull drawing, a modified method developed from hot embossing (Fig. 2C) [5]. In a second saturation step, these micro and nanostructured polymers are exposed to CO_2 at different pressures, temperatures, and durations for the pore production in a high pressure apparatus, whereas the maximum possible temperature is up to 200°C, the maximum pressure is 50 MPa, and the exposure time can vary from seconds over minutes or hours. After

depressurizing, the polymeric porous micro and nano-structures can additionally be thermally treated for fine-tuning of the porous structures.

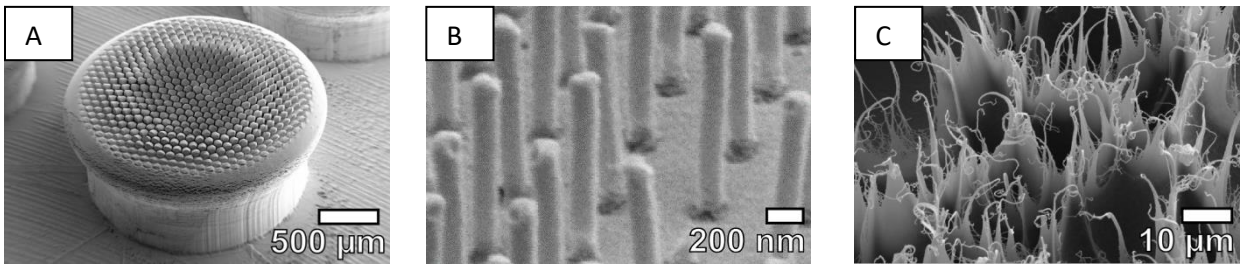

Figure 2. A) Hot embossing for hierarchical microstructures, B) Nanostructured columns of 140 nm diameter with high aspect ratio of 1:10, C) super hydrophobic nanofur produced by hot pull drawing [5].

RESULTS

By the combination of the two described methods several different types of microstructured materials have been produced according to the conceptual approach shown in Figure 3: First, porous structures in different types of polymer films have been produced successfully. Afterwards, porous microstructures with a range of 1 to 300 µm have been obtained. The next challenge has been to achieve a hierarchical pore structure aiming on microstructures with catalytically active nanoparticles and pore gradients in the last step.

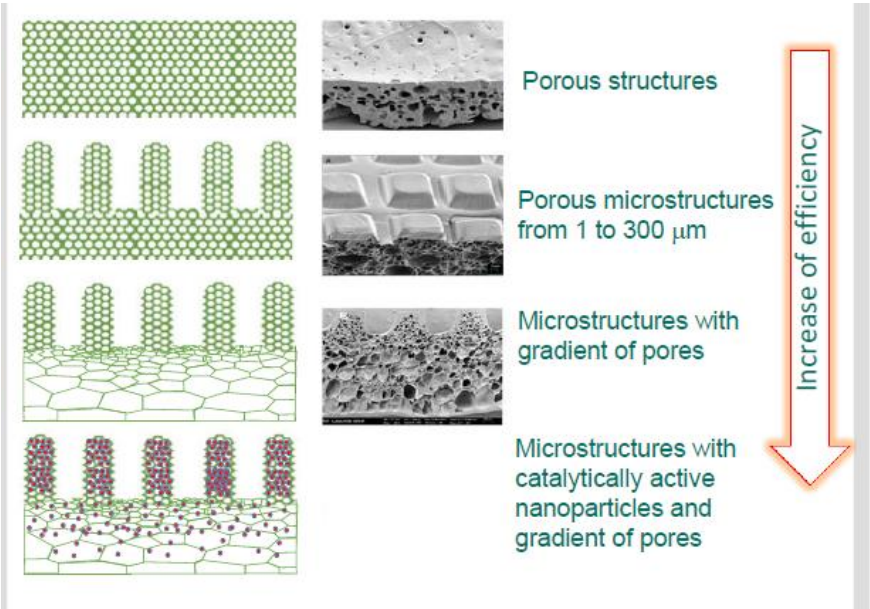

Figure 3. Concept for production of micro and nano structured porous polymers

According to this concept, in first experiments, polystyrene (PS) films without microstructure have been exposed to CO_2 at 5 MPa and 20°C for 15 min. After a thermal post-treatment at 123°C pores in the range of 15 µm to 30 µm have been obtained, but without a completely continuous pore structure. No skin formation has been observed (Figure 4A). The next experiments have been performed with polyurethane (PU) polymers at 7 MPa and 40°C for 2 h. A thermal post-treatment at 115°C has been performed with the following result: pores in the range of 200 to 400 nm with a

surface skin (Figure 4B). The last series has been carried out using Tecoflex TPU polymer (aliphatic polyether-based thermoplastic polyurethane) at 5 MPa and 20°C for 15 min. Without any thermal post-treatment, pores in the range from 2 µm to 40 µm with a continuous pore gradient have been obtained (Figure 4C).

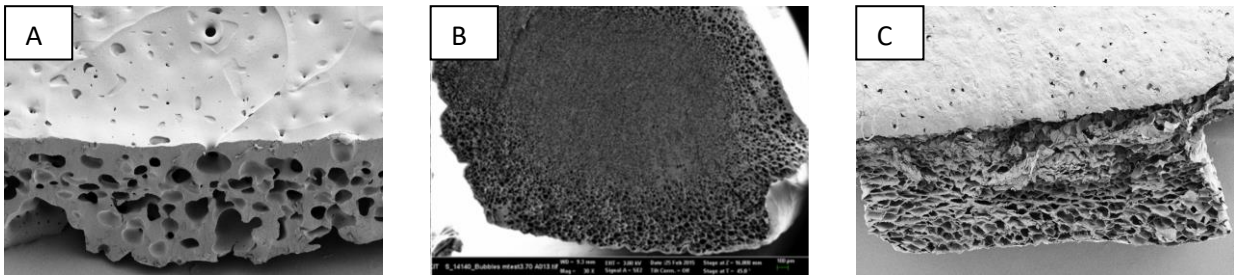

Figure 4. Porous structures in polymer films by exposition to CO_2. A) Polystyrene (5 MPa, 20°C, 15 min, 15-30 µm pores, no skin), B) Polyurethane (7 MPa, 40°C, 2 h, 200-400 nm pores, surface skin) C) Tecoflex TPU (5 MPa, 20°C, 15 min, 2-40 µm, no thermal post-treatment, continuous pore gradient.

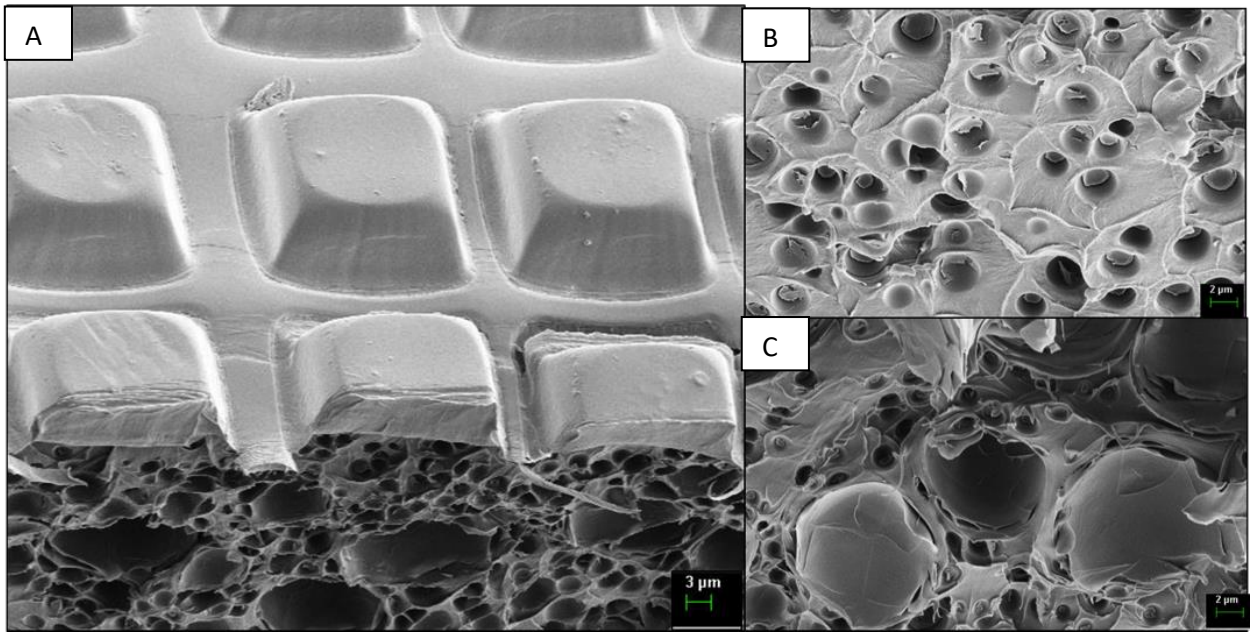

Figure 5. Pores in PMMA microstructure (5-20 µm) obtained by exposition to CO_2 at 5 MPA, 20°C, 15 min. A) survey B) thermal post-treatment with 100°C resulting in 2 µm pores C) thermal post-treatment at 104°C resulting in 10 µm pores.

As soon as these results had been obtained, the production of micro porous structures in subcritical CO_2 has been investigated. Micro columns of PMMA with a dimensioning of 5-20 µm have been produced via hot embossing [6] and then exposed to CO_2 at 5 MPa and 20°C (Figure 5A). The results of a thermal post-treatment at 100°C results in pores of 2 µm (Figure 5B) and at 104°C in pores of 10 µm (Figure 5C). Further experiments showed that a pore range from 200 nm to 10 µm is possible as well as formation of a surface skin and a hierarchical pore gradient, if pressure (5-30 MPa), exposure time (15 min to 24 h) and thermal post-treatment (100°C-105°C) are varied at room temperature (20°C).

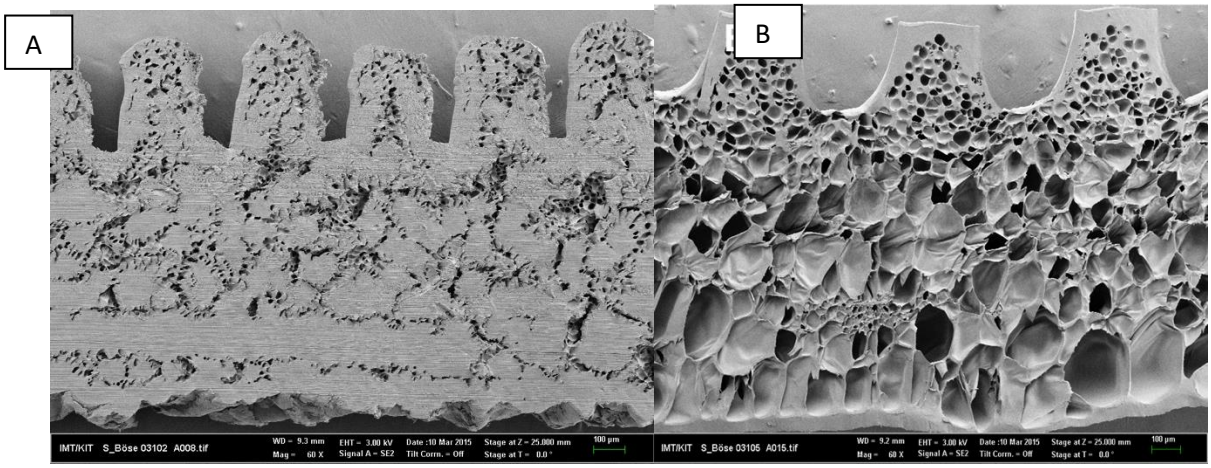

Figure 6. Porous PLA microstructures (columns of 300 µm width) A) with interconnected pores foamed at 4 MPa for 15 min with a thermal post-treatment at 70°C, B) with a pore gradient from 230 µm to 35 µm.

Another approach has shown that bio-degradable thermoplastic materials like Polylactide (PLA), used in medical and food applications [7], can also be microstructured with columns of a width of 300 µm at the following saturation conditions in CO_2: 5MPa-50 MPA, 27°C-44°C, 15 min with a thermal post-treatment at 70°C-90°C. The results are interconnected micro pores in the range of 1 µm-50 µm, with or without pore gradients and a skin on the surface, as shown in Figure 6A. In summary, the experiments demonstrated that saturation in supercritical carbon dioxides at 30 MPa results in pores in the range from 200 nm to 400 nm at a thermal post-treatment afterwards at temperatures between 95°C and 120°C. The sample exhibits a high pore density and uniform pore structures. The surface properties of materials with pores less than 1 µm can vary from hydrophilic to hydrophobic, which enables in general biomedical applications [8].

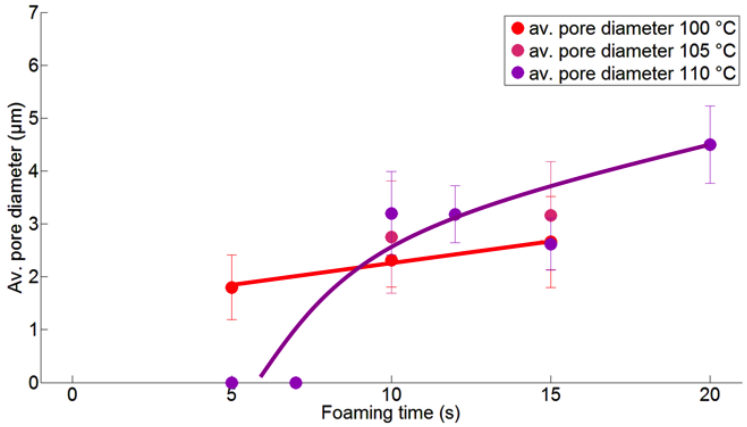

Figure 7. Averaged pore diameter at a CO_2 pressure of 6 MPa at room temperature as a function of thermal post-treatment resulting in pores diameters in the range from 200 nm to 4.5 µm [9].

After many test series with PMMA (type Topacryl 2 New), the relation between pore size, exhibition time in CO_2 and temperature of thermal post-treatment has been analyzed. Figure 7

shows the influence of the time for thermal post-treatment at different temperatures (100°C, 105°C, 110°C) on the pore diameter. The values display an increase in the average pore diameter (and also of the relative total area of pores) with foaming time; here the temperature used for thermal post-treatment shows only a minor effect. In general, the deviation of pore sizes is increased by a higher thermal post-treatment at 110°C (as it can be seen in Figure 8) [9].

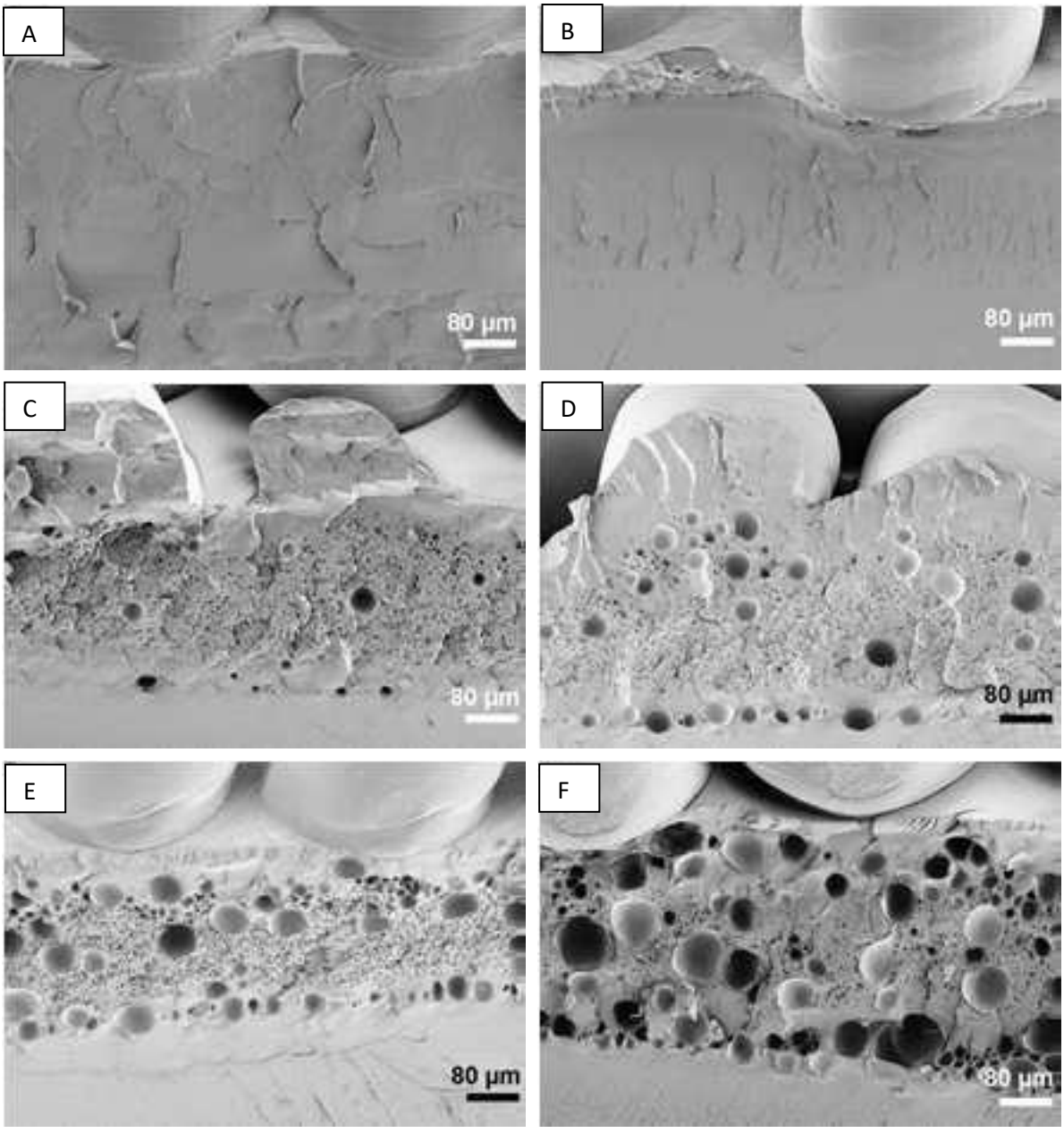

Figure 8. SEM pictures showing the influence of the foaming time at a foaming temperature of 110 °C (saturation pressure of 60 bar). Foaming times: A) 5 s, B) 7 s, C) 10 s, D) 12 s, E) 15 sec, F) 20 s. [9].

Micro to nano porous polymers with tunable stiffness have been inspired by structural hierarchies and the related excellent mechanical properties of biological materials, as exhibited e.g. by adhesive hairs with a hierarchical structure as known from Geckos [10] and the ladybird beetle (*Coccinella septempunctata*) [11]. Also pomelo peels (*Citrus maxima*) survive falls from heights

above 10 m without any visible external damage [12]. These examples inspired the production of smoothly graded micro to nano porous structure from a thermoplastic PMMA polymer. The viscoelastic properties for the different pore sizes were investigated and interestingly, the storage modulus was observed to increase with increasing pore-area fraction showing that the elastic properties can be tuned in a non-chemical way by adjusting the pore size gradient in polymers. Porous PMMA films with a controlled gradient of the pore size were fabricated and have proven that even the viscoelastic properties of thermoplastic polymers can be tuned by adjusting smoothly graded micro to nano structures inspired by structural hierarchies and the related excellent mechanical properties of biological materials [3].

Recently, ultra-thin porous PMMA films exhibiting a bright white color, as known from the white beetle of the genus *Cyphochilus*, can be produced by this saturation method using CO_2 followed by a thermal post-treatment at different conditions [4]. The bio-inspired white films do not lose their whiteness during further shaping, allowing for various applications

CONCLUSION

According to the conceptual approach (Figure 3), different types of polymer films (PMMA, PS, PU, Tecoflex TPU, PLA) have been used to produce successfully different types of porous structures ranging from nano to micro size, but also structures with hierarchically pore gradients (Figure 4, Figure 5, Figure 6). Hierarchically porous polymers combining different pore structures and hierarchies are desirable for different technical applications in separation and catalysis [13, 14, 15]. It has been shown that the process influencing parameters for the high pressure saturation step (pressures, temperature and exposition time in subcritical or supercritical CO_2) as well as for the following thermal post-treatment step (temperature and time) can be varied in order to obtain optimal pore sizes and gradients. A key factor for potential technical applications is the connectivity of pores without a skin on the surface. It has been demonstrated that with the applied technique such structures can be produced (Figure 4A). The so far developed techniques and the achieved results are a base for future high-performance materials with a broad spectrum of applications from separation over catalysts for chemical reactions to medical implants [7, 13, 14, 15, 16]. Also, adjustment of elastic moduli or production of bright white films is possible.

ACKNOWLEDGEMENTS

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