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ABSTRACT BOOK

3D printing of porous polymer structures with digital light processing technology

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Introduction

Three dimensional (3D) printing, as a type of additive manufacturing of unique structures, became a major field in research in the past two decades. Most of the 3D printers use a layer-by-layer approach to create objects from either plastic, metal or even ceramic materials. A commonly used technique is digital light processing (DLP), where each layer is created by projecting light onto a two-dimensional cross section (Fig. 1a) [1]. A printed polymer resin is made up of several components, such as (macro)monomers, initiators, stabilizers, and pigments. The most commonly used macromonomers are (di)acrylates and (di)methacrylates, where the cross-linking mechanism is free radical polymerization [2]. In our research we prepared functionalized macroporous structures (scaffolds) by DLP printing. The scaffolds developed were based on poly(ethylene glycol) diacrylate (PEGDA) to which glycidyl methacrylate (GMA) was added for epoxy functionalization.

Experimental

Poly(ethylene glycol) diacrylate and pentaerythritol triacrylate (PETA) were used in the 3D printing. Glycidyl methacrylate (GMA) was also included to provide epoxy functionalization. The optimal composition of the resin was determined by adjusting the concentration of the components to achieve better mechanical properties and shorter printing time. The mechanical properties were measured by tensile testing. 3D printed porous structures were also prepared by using the optimal concentration. To enhance the lateral resolution, we used Sudan red dye and varied its concentration to achieve the smallest pore size possible, while minimizing exposure time. To measure the pore size of the printed samples, digital optical microscopy (DOM) was used. The effect of the photoabsorbent concentration on the mechanical properties of the samples was studied. To measure the concentration of the epoxy groups on the surface of the scaffolds the epoxy groups were reacted with L-tryptophan, and fluorescence was induced by UV irradiation. In another method, we reacted the epoxy-groups with benzylamine, and quantitative analysis was performed by using UV-VIS spectroscopy. The presence of the epoxy groups was also proven by Fourier transformation IR spectroscopy (FTIR). In this study we also used industrial resins such as PEGDA with black pigments to achieve low pore sizes. The printing time and pore size were changed and the characteristics of the printed scaffolds were investigated.

Results and discussion

The addition of PETA decreased, while GMA increased the polymerization time. By adding PETA the polymerization became so intense that vapor formation could be seen. The tensile tests proved that while the addition of PETA increases the Young's modulus and the tensile strength, the fracture strain decreased and the samples broke easily. Due to this the use of PETA was disregarded. The addition of Sudan red dye made it possible to create honeycomb

structures with pores of 300-400 μm (Fig. 1b), but it had a negative effect on the mechanical properties. The 3D printing process was also optimized. The Young's modulus, the fracture strain and the tensile strength were 14.6 MPa, 10.7% and 1.5 MPa, respectively. The presence of the epoxy groups on the surface was proven by all three methods.

3D printing was also done by using an industrial raw material and porous objects with 200 μm pore size could be obtained. The optimization of the printing process included changing the exposure time, the pigment/dye concentration, the size and pattern of the supports on the structure. It was noted that resins with higher pigment concentrations have longer printing time. In this study the exposure time varied from 4 s to 12 s. For the first 4-8 layers the irradiation time was increased by 1 s.

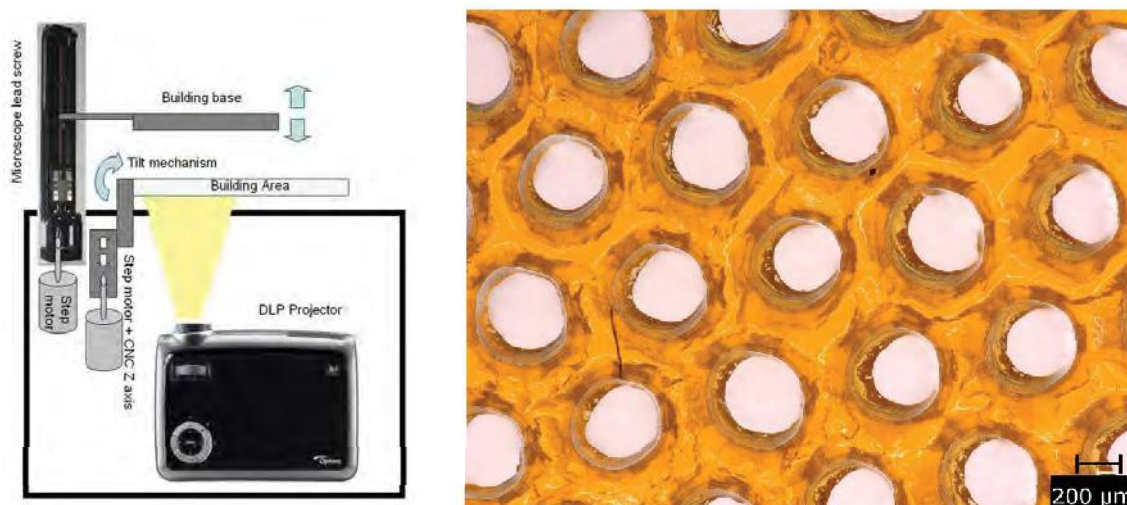


Fig. 1. a) Build-up of the used DLP 3D printer b) 3D printed macroporous structure

Conclusions

In our work we introduced a versatile and flexible method for printing functionalized polymer structures with various pore sizes. We developed a new PEGDA/GMA resin which is applicable in tissue engineering or other biotechnological research. The printed porous acrylate structures can be pyrolyzed to convert them into a carbon framework, which may have high electrical conductivity, so they could be used as electrodes for biological sensors and batteries.

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