

3D PRINTED BIOCOMPATIBLE POLYMERS

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3D printing by lithography-based additive manufacturing technologies enable the generation of highly complex 3D structures with very high resolution. This attracted the interest of modern medicine as the regeneration of defected tissue demands biomaterial scaffolds with patient-specific geometries. The vision is to be able to fill the defects in tissues or whole organs with tailor-made, biocompatible polymeric constructs, which promote the regeneration of the tissue or the organ.

Lithography-based additive manufacturing technologies (L-AMTs) base on the curing of liquid formulations in a layer-by-layer manner using light as trigger. Crucial ingredients of such formulations are the monomer, which bears photopolymerizable groups (mainly double-bonds), and the photoinitiator that initiates the polymerization by the generation of reactive species (mainly radicals) when exposed to light.

Important design factors for photopolymers used as tissue regeneration scaffolds are the mechanical properties of the material (ideally matching the properties of the tissue), the biodegradation behavior (which is ideally in-sync with the pace of the regeneration of new tissue), and the biocompatibility, which render the material to promote the attachment of cells and to support the growth of tissue. Furthermore, all components, incl. degradation products, should have a very low toxicity.

In the last decade, considerable progress was made in the field of bone tissue regeneration using 3D scaffolds based on vinyl ester monomers printed digital light processing (DLP) based L-AMTs. The low toxicity of vinyl esters (esp. compared to acrylates), their favorable degradation products - acetaldehyde and polyvinyl alcohol - and their tune-able reactivity (by thiol-ene chemistry) made them a versatile material platform in this field. For soft tissue regeneration hydrogels were found to be promising material candidates. Their high compliance, combined with their permeability for nutrients making them an ideal model system to study structure-properties relationships of the extracellular matrix (ECM). In order to match the fine structural features of native ECM it is necessary to employ two-photon-lithography (2PL) with resolutions > 1 μm . Derivatives of collagen and hyaluronic acid, both main components of the ECM, where used as hydrogel precursors (modification with methacrylates and vinyl esters) to encapsulate living cells in 3D scaffolds by 2PL. By incorporation of photo-labile groups (e.g., o-nitrobenzylester) into the hydrogel network photo-cleavage of formed crosslinks by the two-photon-process is enabled and channels for the spreading of cells can be created.

Taken together these material platforms accompanied by different L-AMTs, DLP-based for resolutions in the range 20 μm and two-photon-technology for the submicron range, allow the production of tailor-made biomaterial scaffolds for the regeneration of tissue and the spatial-temporal control of hydrogel properties in the presence of living cells to study the behavior of living cells in different micro-environments.