Vat 3D printable materials and post-3D printing procedures for the development of engineered devices for the biomedical field

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Abstract

3D printing technology is changing how objects are designed and manufactured by gradually introducing novel production concepts. Indeed, 3D printing is considered as one of the fundamental pillars of the so-called Industry 4.0. It enables the fabrication, in a short time, of bespoke parts with *quasi* any geometry from a digital model and without requiring tooling or expensive equipment. 3D printing techniques are based on the layer-by-layer spatial-controlled joining of materials, a concept that can be applied to metallic powders, ceramic slurries, polymers, and composites in different conditions, i.e., liquid, gel, powder, or solid filaments. Moreover, 3D printing allows the fast production of customized objects and, at the same time, a better way of using raw materials, generating economic savings.

In the biomedical field, 3D printing has found a particular ground for producing customized goods such as medical implants, biological models, and biomedical analytical systems. In this scenario, polymers' 3D printing is largely exploited for medical applications thanks to the relatively wide availability of printable polymers, offering a palette of different properties. Furthermore, they can also be processed by cost-affordable printer machines. All this has gradually led doctors, experts, and scientists to approach 3D printing for many particular biomedical purposes where personalized devices or implants are promptly required.

A clear example was observed during the recent pandemic outbreak related to COVID-19, where customized pieces were on-demand and rapidly produced near hospitals, demonstrating how polymeric 3D printing can play a fundamental role in crisis moments. Nevertheless, to keep up with the rise of 3D printing in the biomedical field, new materials must be developed to satisfy basic biomedical properties, e.g., biocompatibility. The current

market for printable polymers shows that only a few are considered biocompatible, and post-printing treatments play a crucial role in reducing the potential toxic agents.

The investigations presented in this dissertation focus on the development of custom-made photosensitive polymers or photopolymers for light-based 3D printing applications, also noted as vat polymerization, intending to produce bespoke objects with biomedical features. By combining appropriate materials during the printable polymer preparation and the freedom of design given by 3D printing, unique structures can be produced with interesting bioproperties; the following chapters will present different approaches to achieve such purposes. An overview of the 3D printing technology, its achievements, and challenges, focusing on the light-induced techniques, is first reported in Chapter 1 of this thesis. It follows in Chapter 2, a literature review on polymeric 3D printing applications in the biomedical field.

The first experimental part is based on preparing and testing commonly-used photopolymers for vat 3D printing to produce parts for biological studies (Chapter 3, Part I). Post-printing treatments will also be explored to eliminate the potentially toxic elements from the printed parts, thus enhancing cell lines' biocompatibility. Other polymeric systems based on acrylate-polydimethylsiloxane (PDMS) resins are also presented to print complex-shaped and three-dimensional structures with good printing resolution (Chapter 3, Part II). In this case, the specific idea is to fabricate 3D printed PDMS-based microfluidic chips with characteristics similar to the conventional PDMS material used for microchip fabrication. The final goal consists of obtaining parts with great optical features, high chemical stability, and good mechanical properties.

Chapter 4 reports the second experimental contribution based on the investigation of specific post-printing protocols to induce surface modification on the printed parts, intending to expand their bioproperties. The changes in the printed objects' properties will be assessed by taking advantage of some reactive functional groups exposed on their surface after 3D printing. These functional groups can be used to link additional molecules of biological interest. The surface functionalization can proceed during the necessary post-curing step via UV-induced grafting polymerization techniques, even in close microfluidic devices (Chapter 4, Part I), or via microwave radiation (Chapter 4, Part II).

The last experimental part focuses on exploiting an exclusive additive during the photopolymer preparation for increasing the printed parts' functionality (Chapter 5). A custom-made photopolymer is prepared by integrating a functional dye to obtain 3D printed structures with inner properties such as convenient optical characteristics, adequate light-guiding performances, and high sensitivity to different environments.

The research findings reported in this manuscript describe the efforts to shorten distances between the potential medical application of 3D printing and the available polymeric materials to produce more reliable and suitable biomedical parts. This doctoral dissertation's main idea is to enlarge the palette of the processable polymers with biological characteristics; each of the developed materials and methods reported here might be used as novel tools for biomedical purposes, particularly in point-of-a-care medicine.