Doctoral Dissertation
Doctoral Program in Electrical, Electronics & Communications Engineering (36th Cycle)

Introducing Advanced Conductors and Semiconductors in 3D polymeric composites for further electronic & photocatalytic applications

Alejandra Salas

* * * * * *

Supervisors
Prof. Cocuzza Matteo
Prof. Pirri Candido

Politecnico di Torino

September 28, 2024

Abstract

Additive Manufacturing (AM) permits the development of complex printed architectures, rendering them from a computer-aided design (CAD) towards a physical structure. This technology allows the combination of multiple scientific approaches, starting from the chemistry in the materials, the kinetics & processing of the solidification reactions, and the AM technique applied, which variables would strictly depend on the final product's desired properties. 3D polymeric printing can enclose a whole set of science behind the spatially controlled solidification of its monomeric/oligomeric parts depending on the method chosen, such as fused filament fabrication (FFF), selective laser melting (SLM), inkjet, and vat photopolymerization methods that can include great printing fidelity (<35 μm) and fast printing times (<1h) like Stereolithography (SL) or Direct Light Processing (DLP). Nowadays, for the latter, the market offers inexpensive and more commercial options such as Liquid Crystal Display (LCD) technology.

The photopolymeric resin formulations normally include a polymeric matrix and embedded additives that can provide specific properties as will be explained in this thesis work. Usually, structural characteristics like flexibility and rigidity are attributed to the polymeric matrix, as well as reactivity or even the capacity to withstand extreme conditions depending on the chosen monomers/oligomers. Regarding the additives, there is a whole set of fillers, colorants, and radical scavengers that can be included in the formulation to adjust or incorporate functional properties to the printed structure for specific applications.

The scope of this Ph.D. thesis was to study the inclusion of advanced conductor/semiconductor materials as fillers in 3D printable polymeric matrixes to develop 3D structures for electronic or photocatalytic applications. The use of DLP and LCD was selected as printing technology, allowing fast material processing in their liquid state, and acquiring high-resolution 3D objects. Both printing methods employ photopolymerization, defined as the assembling of monomers/oligomers initiated by the reaction of a photoinitiator with incident light. The reaction starts when a projection of the light pattern from the layer to print arrives on the screen which is in contact with the vat, and slices are rapidly cured, producing a 3D structure in a layer-by-layer process. However, a load of additives and specifically fillers may limit the light absorption of the photoinitiator due to photoblocking activity or light scattering, leading to a decrease in the reaction kinetics affecting the printing process.

In the first part of the research, the development of polymeric MXene/composites was investigated for the later production of 3D-printed objects applied in electronics. A MXene being a 2D material based on transition metal carbides, carbonitrides, or nitrides with huge research interest given their novelty, and properties such as high electrical conductivity, hydrophilicity, and thermal endurance. The MXene composition used in this study is $Ti_3C_2T_z$, to deliver its electrical properties to build 3D conductive objects by photopolymerization.

These were then introduced into a monomer formulation of Bisphenol A dimethacrylate (BPA-dma) and Trimethylolpropane triacrylate (TMPTA), whose reactions kinetics was studied by photorheology, while chemical characterization and IV measurements were performed to study the material properties. The choice of these monomers was based on their compatibility with an annealing post-process, which was further exploited to enhance the electric conductivity of the 3D structures.

The innovation of this study relies on the use of MXenes in DLP as a printing method and the study of the influence of Titanium carbide ($Ti_3C_2T_z$) inside the vat photopolymerization. Also, in the exploration of how its properties are affected when including them in 3D objects and submitting them to high temperatures when using the annealing as post-process.

In the second part of the research, the use of a specific advanced semiconductor photocatalytic material was explored also as filler in DLP and LCP printing methods for the development of 3D printed composites. The semiconductor chosen being a hybrid system, composed of phenyl carbonitride as the organic part and TiO_2 in its anatase phase as the inorganic one, forming a heterojunction of Phenyl carbonitride and Titanium oxide ($PhCN/TiO_2$) known for its great performance in photocatalysis. The purpose of this investigation was to explore the inclusion of $PhCN/TiO_2$ in 3D printing vat photopolymerization and how its photocatalytic performance was affected when included in the printed structures. As a polymeric matrix, a polyethylene glycol diacrylate (PEGDA) formulation was considered adding a silane monomer 3-(trimethoxy silyl)propyl methacrylate (TMSPM) to improve mechanical resistance and the ability of the matrix to withstand the photocatalysis reaction. Furthermore, comparing the best method to include $PhCN/TiO_2$ in 3D printing and translating its photocatalytic activity which was evaluated by the degradation under visible light irradiation of Rhodamine B (RhB), the material was considered also under a coating strategy. For this, the silane monomer was used as a coupling agent between the organic matrix and the inorganic part of the hybrid system, via the sol-gel technique.

The innovation of this part is the inclusion of this hybrid system inside the vat photopolymerization and as a post-treatment, for the analysis of its application as photodegradation capacity at visible light. Also, its influence in the PEGDA system, and how by adding TMPSM in the matrix properties are improved to withstand the inside reactions. In the last set of experiments, a glassy polymeric composite approach was also utilized for its inertness over extreme environments with the same polymeric matrixes, which is going to be introduced in the appendix as it did not work effectively.

Throughout the Ph.D. and this manuscript, the development of different polymeric matrixes and their optimization was done to improve the quality of the final composite when including the fillers in the formulation. 3D printing can serve for fabricating objects with added values, in combination with multi-scientific approaches. The design can applied in a wide set of application fields as seen during these years, as electronics and photocatalysis.