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Development of aluminum-phosphate hybrid materials via sol-gel route for additive manufacturing of photonic materials

**Thèse en cotutelle
Doctorat en Physique**

Gabriel Toshiaki Tayama

Sous la direction de :

Prof. Tigran Galstian, directeur de recherche

Prof. Younes Messaddeq, directeur de cotutelle

Ph.D. Silvia Helena Santageneli, codirectrice de cotutelle

GABRIEL TOSHIAKI TAYAMA

**Development of aluminum-phosphate hybrid materials via sol-gel
route for additive manufacturing of photonic materials**

Thesis in cotutelle with Université Laval – Quebec –
Canada presented to the Institute of Chemistry,
Universidade Estadual Paulista, to obtain the
degree of Doctor in Chemistry

Brazilian advisor: Younes Messaddeq

Brazilian co-advisor: Silvia Helena Santagneli

Canadian advisor: Prof. Tigran Galstian

Araraquara

2023

T236d	Tayama, Gabriel Toshiaki Development of aluminum-phosphate hybrid materials via sol-gel route for additive manufacturing of photonic materials / Gabriel Toshiaki Tayama – Araraquara: [s.n.], 2023 265 p.: il. Thesis (doctor) – Universidade Estadual Paulista, Instituto de Química Advisor: Younes Messaddeq Co-advisor: Silvia Helena Santagneli 1. Three-dimensional printing. 2. Photonics. 3. Phosphates. 4. Lanthanides. 5. Optical properties. I. Title.
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IMPACTO POTENCIAL DESTA PESQUISA

Os potenciais impactos decorrentes deste projeto de doutorado compreendem o aprofundamento e nacionalização do conhecimento em manufatura aditiva aplicada a síntese de materiais obtidos a partir da rota sol-gel, que tem ganhado destaque nos últimos anos, dada sua aplicação na manufatura de vidros inorgânicos e materiais híbridos. Dessa maneira, espera-se que essa tese possa contribuir no desenvolvimento desse setor industrial estratégico, com a geração de empregos e propriedade intelectual, fornecendo infraestrutura para uma miríade de aplicações de alta tecnologia.

POTENTIAL IMPACT OF THIS RESEARCH

The potential impacts arising from this doctoral project include the deepening and nationalization of knowledge in additive manufacturing applied to the synthesis of materials obtained from the sol-gel route, which has gained prominence in recent years, given its application in the manufacture of inorganic glasses and hybrid materials. In this way, it is expected that this thesis can contribute to the development of this strategic industrial sector, with the generation of jobs and intellectual property, providing infrastructure for a myriad of high-tech applications.

IMPACT POTENTIEL DE CETTE RECHERCHE

Les impacts potentiels découlant de ce projet de doctorat comprennent l'approfondissement et la nationalisation des connaissances en fabrication additive appliquées à la synthèse de matériaux obtenus à partir de la route sol-gel, qui a pris de l'importance ces dernières années, compte tenu de son application dans la fabrication de verres inorganiques et de matériaux hybrides. De cette façon, on s'attend à ce que cette thèse puisse contribuer au développement de ce secteur industriel stratégique, avec la création d'emplois et la propriété intellectuelle, fournissant une infrastructure pour une myriade d'applications de haute technologie.

CERTIFICADO DE APROVAÇÃO

TÍTULO DA TESE: "Development of aluminum-phosphate hybrid materials via sol-gel route for additive manufacturing of photonic materials"

AUTOR: GABRIEL TOSHIKI TAYAMA

ORIENTADOR: YOUNES MESSADDEQ

COORDINADORA: SILVIA HELENA SANTAGNELI

Aprovado como parte das exigências para obtenção do Título de , pela Comissão Examinadora:

Prof. Dr. YOUNES MESSADDEQ (Participação Virtual)
Departamento de Química Analítica, Físico-Química e Inorgânica / Instituto de Química - UNESP - Araraquara

Prof. Dr. TIGRAN GALSTIAN (Participação Virtual)
Centre d'Optique Photonique et Laser -
Université Laval

Prof. Dr. MARCELO NALIN (Participação Virtual)
Departamento de Química Analítica, Físico-Química e Inorgânica / Instituto de Química - UNESP - Araraquara

Prof. Dr. PETER MCBREEN (Participação Virtual)
Université Laval - Quebec

Prof. Dr. THIERRY CARDINAL (Participação Virtual)
Institut de Chimie de la Matière Condensée de Bordeaux - UB - França

Araraquara, 12 de outubro de 2023



CURRICULUM

Personal Data

Name: Gabriel Toshiaki Tayama

Name in bibliographic citations: Tayama, G.T.

Address: Universidade Estadual Paulista “Júlio de Mesquita Filho”

Instituto de Química

Departamento de Química Geral e Inorgânica

Rua Francisco Degni 55

Quitandinha – Araraquara – SP

CEP: 14800-900

Phone Number: (581) 849-3450

E-mail Address: gabrieltayama@gmail.com, gabriel.tayama.1@ulaval.ca, gabriel.tayama@unesp.br

Academic Education

2013-2017: Bachelor in Materials Engineering

Universidade Federal de São Carlos (UFSCar)

Bibliographic Production

Journal Publications:

G. T. Tayama, S. H. Messaddeq, S. H. Santagneli, and Y. Messaddeq, “Correlation Between Critical Energy, Penetration Depth, and Photopolymerization Kinetics in Aluminum-Phosphate-Silicate Hybrid Materials for Vat-Photopolymerization,” *Macromolecules*, XXXX, XXX, XXX-XXX, Mai. 2023, doi 10.1021/acs.macromol.3c00363.

G. T. Tayama, S. H. Santagneli, M. de Oliveira Junior, and Y. Messaddeq, “Understanding the Microstructure Connectivity in Photopolymerizable Aluminum-Phosphate-Silicate Sol–Gel Hybrid

Materials for Additive Manufacturing,” *J. Phys. Chem. C*, p. acs.jpcc.2c08027, Jan. 2023, doi: 10.1021/acs.jpcc.2c08027.

M. Posternak, G. T. Tayama, S. H. Messaddeq, and Y. Messaddeq, “Process modeling of laser scanning vat-photopolymerization operating under intermittent exposure conditions,” *Addit. Manuf.*, vol. 60, p. 103234, Dec. 2022, doi: 10.1016/j.addma.2022.103234.

G. T. Tayama, S. H. Santagnelli, H. Eckert, S. Pawsey, and Y. Messaddeq, “Preparation and Structural Characterization of New Photopolymerizable Transparent Aluminum-Phosphate Hybrid Materials as Resins for 3D Printing,” *J. Phys. Chem. C*, vol. 124, no. 46, pp. 25621–25631, Nov. 2020, doi: 10.1021/acs.jpcc.0c08289.

Conference Presentations:

G. Tayama, S. Santagnelli, S. H. Messaddeq, T. Galstian, and Y. Messaddeq “Compositional dependency of 3D printing parameters in silica-aluminum-phosphate hybrid materials” Oral session presented at: Solgel 2022, July 24-29th, Lyon, France

G. Tayama, S. Santagnelli, M. O. Junior, and Y. Messaddeq “Deep understanding on the formation of silica-aluminum-phosphate hybrid materials using solid-state NMR”. Poster session presented at: Sol-gel 2022, July 24-29th, Lyon, France

G. Tayama, S. Santagnelli, and Y. Messaddeq “Hybrid sol-gel as precursors towards additive manufacturing of photonic”. Poster session presented at: 2nd Photonics National Institute for Science and Technology, February 12-15th, Araraquara, Brazil

G. Tayama, S. Santagnelli, and Y. Messaddeq “Hybrid sol-gel inks for stereolithography of aluminum-phosphate hybrids”. Poster session presented at: 25th International Conference on Glasses 2019, June 9-14th, Boston, USA

G. Tayama, L. S. Gallo, and E. D. Zanotto “Glass-ceramics of high mechanical strength”. Poster session presented at: X BraSGlass – Brazilian Symposium on Glass and Related Materials, October 26-30th, São Carlos, Brazil

ABSTRACT

Additive manufacturing (AM) is a technology with great potential for use in photonic applications because it overcomes the limitations of traditional manufacturing methods. Among the various AM techniques available, the vat-photopolymerization (VPP) is one of the few that meets the requirements for photonics manufacturing. However, one of the main challenges hindering the widespread adoption of VPP in optical device manufacturing is the limited availability of materials compatible with VPP techniques.

The aim of this thesis was to develop, elucidate the structure of, fabricate via additive manufacturing, and study the optical properties of 3D printed parts of aluminum-phosphate hybrid materials. These materials were developed using the sol-gel route as candidates for the fabrication of active and passive photonic devices. These materials were additive manufactured via VPP using a custom-made AM system operating under intermittent exposure conditions. We developed a mathematical model describing the exposure profile output by this custom-made VPP setup, since its operating principle greatly differs from commercial platforms. Then, these new materials were 3D printed after characterizing their VPP parameters and photopolymerization kinetics. Lastly, we examined the optical homogeneity and anisotropy of additive manufactured elements from these materials. These goals were explored throughout five scientific publications, composing the five chapters of this thesis.

In our first contribution, we synthesized photopolymerizable aluminum-phosphate sols, that were polymerized to result in organic-inorganic hybrid (OIH) materials composed by poly (2-hydroxyethyl methacrylate) chains with aluminum-phosphate groups covalently bonded to the polymeric backbone. These inorganic units provide numerous crosslinkers, resulting in a highly interconnected and interlocked inorganic/organic structure. The OIH materials were optically transparent between the 420 nm - 1100 nm, however, these materials showed low transmittance in the near-infrared region (NIR) due to the high organic content of these matrices.

In a second contribution, we modified the synthesis route to achieve aluminum-phosphate-silicate OIH materials with higher inorganic mass concentration and improved transmittance in the NIR. We investigated in-depth the structure of these materials by means of solid-state NMR and observed that the inorganic network is formed by aluminum-phosphate units interconnected by silicate chains.

The chemical environment of the phosphate and aluminate sites could be tuned based on the aluminum to phosphorus ratio, allowing the structure to be tailored in order to enhance the lanthanide ions hosting ability of these materials. These structural features present these materials as potential candidates to immobilize lanthanide ions for developing active optical components.

In a third contribution, we developed and tested a mathematical model describing the exposure profile outputted by the custom-built printer employed in this work, allowing us to model the laser-resin interaction in this equipment, and to correlate the printing parameters measured for our materials with those of commercial AM setups. Furthermore, we identified that this printing system can, theoretically, print faster compared to commercial platforms under specific conditions of beam diameter and overlap between pulses.

In a fourth contribution, we explored the additive manufacturing of the aluminum-phosphate-silicate resins. The evolution of the 3D printing parameters of these materials (critical energy and penetration depth), and of the photopolymerization kinetics with light intensity and silicate concentration was studied. These results indicate the shift of critical conversion towards higher polymerization degree as the concentration of silicate increases, which was associated to a higher tendency towards cyclization. These results were employed to validate a photochemical model published in the literature describing the laser-resin interaction in VPP systems, elucidating the link between critical energy and photopolymerization kinetics.

In our last contribution, we studied the refractive index distribution and the presence of optical anisotropies in 3D printed lines. We identified that the 3D printed parts are optically homogenous, despite the presence of a gradient of polymerization degree associated to the penetration of the laser into the resin and the beam profile. Optical anisotropies were identified, and polarized micro-Raman measurements indicate that the birefringence arises from the shear stress perpendicular to the scan direction due to the inflow of monomer towards the polymerization spot.

RESUMO

A manufatura aditiva (MA) é uma tecnologia com grande potencial para aplicações em fotônica, pois contorna as limitações impostas por métodos tradicionais de manufatura. Entre as várias técnicas de MA disponíveis, a fotopolimerização em cuba (VPP) é uma das poucas que atende os requisitos de tolerância presente na fabricação de dispositivos fotônicos. No entanto, um dos principais desafios que impedem ampla adoção da VPP na fabricação de dispositivos ópticos é a baixa disponibilidade de materiais processáveis com as técnicas de VPP.

O objetivo desta tese foi desenvolver, elucidar a estrutura, fabricar via manufatura aditiva e estudar as propriedades ópticas de peças impressas 3D de materiais híbridos de alumínio-fosfato. Esses materiais foram desenvolvidos utilizando a rota sol-gel como candidatos para a fabricação de dispositivos fotônicos ativos e passivos via impressão 3D. Esses materiais foram processados via VPP usando um sistema MA customizado, operando sob condições de exposição intermitente. Foi desenvolvido e testado um modelo matemático descrevendo o perfil de exposição produzido por esse sistema VPP customizado, uma vez que seu princípio operacional difere daquele de plataformas comerciais. Em seguida, os parâmetros de impressão 3D e a cinética de fotopolimerização desses novos materiais foram estudados, permitindo sua impressão 3D. Por fim, foi estudado a homogeneidade óptica e a presença de anisotropias ópticas em partes produzidas por MA desses materiais. Esses objetivos foram explorados ao longo de cinco publicações científicas, compondo os cinco capítulos desta tese.

Em nossa primeira contribuição, sintetizamos soluções fotopolimerizáveis de alumínio-fosfato, resultando em materiais híbridos orgânico-inorgânicos (HOI) compostos por cadeias de poli (2-hidroxietil metacrilato) com grupos alumínio-fosfato covalentemente ligados ao esqueleto polimérico. Essas unidades inorgânicas atuam como ligações cruzadas, resultando em uma estrutura inorgânica-orgânica altamente interconectada e interligada. Os materiais obtidos são totalmente transparentes entre 420 nm - 1100 nm, porém possuem baixa transmitância na região do infravermelho próximo (NIR) devido ao alto teor orgânico dessas matrizes.

Em uma segunda contribuição, modificamos a rota de síntese para obter materiais HOI de alumínio-fosfato-silicato com maior teor de massa inorgânica e melhor transmitância no NIR. Investigamos em detalhe a estrutura desses materiais por meio de RMN de estado sólido e

observamos que a rede inorgânica é formada por unidades de alumínio-fosfato interligadas por cadeias de silicato. O ambiente químico dos sítios de fosfatos e alumínio podem ser modificados por meio da razão alumínio para fósforo, permitindo que a estrutura seja otimizada para a introdução de íons lantanídeos. Essas características estruturais apresentam esses materiais como potenciais candidatos à imobilização de íons lantanídeos para o desenvolvimento de componentes ópticos ativos.

Em uma terceira contribuição, desenvolvemos e testamos um modelo matemático descrevendo o perfil de exposição produzido pela impressora personalizada empregada neste trabalho, permitindo-nos modelar a interação laser-resina e correlacionar os parâmetros de impressão medidos para nossos materiais com aqueles de plataformas comerciais de MA. Além disso, identificamos que este sistema de impressão pode, teoricamente, imprimir mais rápido comparado a plataformas comerciais, desde que condições específicas de diâmetro do feixe e sobreposição entre pulsos sejam atendidas.

Em uma quarta contribuição, exploramos a manufatura aditiva das resinas de alumínio-fosfato-silicato. Foi estudada a evolução dos parâmetros de impressão 3D desses materiais (energia crítica e profundidade de penetração) e da cinética de fotopolimerização com a intensidade de luz e a concentração de silicato. Os resultados obtidos indicaram um aumento da conversão crítica das resinas com o aumento da concentração de silicato, o que estaria associado a uma maior contribuição da reação de ciclização. Esses resultados foram empregados para validar um modelo fotoquímico descrevendo a interação laser-resina em sistemas VPP publicados na literatura, elucidando a relação entre energia crítica e cinética de fotopolimerização.

Em nossa última contribuição, estudamos a distribuição do índice de refração e a presença de anisotropias ópticas em linhas impressas 3D. Foi verificado que as peças impressas em 3D são opticamente homogêneas, apesar da presença de um gradiente de grau de polimerização associado à penetração do laser na resina e do perfil do feixe. Anisotropias ópticas foram identificadas, e medidas de espalhamento micro-Raman polarizado indicaram que a birrefringência é oriunda da tensão de cisalhamento perpendicular à direção da varredura causada pelo influxo de monômero em direção ao centro da polimerização.

RESUME

La fabrication additive (FA) est une technologie à fort potentiel d'utilisation dans les applications photoniques car elle surmonte les limites des méthodes de fabrication traditionnelles. Parmi les différentes techniques de FA disponibles, la photopolymérisation en cuve (VPP) est l'une des rares à répondre aux exigences de la fabrication photonique. Cependant, l'un des principaux défis qui entravent l'adoption généralisée du VPP dans la fabrication de dispositifs optiques est la disponibilité limitée de matériaux compatibles avec les techniques VPP.

L'objectif de cette thèse était de développer, d'élucider la structure, de fabriquer via la fabrication additive et d'étudier les propriétés optiques de pièces imprimées en 3D de matériaux hybrides aluminium-phosphate. Ces matériaux ont été développés par voie sol-gel comme candidats pour la fabrication de dispositifs photoniques actifs et passifs. Ces matériaux ont été fabriqués via VPP en utilisant un système AM sur mesure fonctionnant dans des conditions d'exposition intermittentes. Nous avons développé un modèle mathématique décrivant le profil d'exposition produit par cette système VPP, car son principe de fonctionnement diffère grandement des plateformes commerciales. Ensuite, les paramètres VPP et la cinétique de photopolymérisation de ces nouveaux matériaux ont été caractérisés, de façon à démontrer leur impression 3D. Enfin, nous avons examiné l'homogénéité optique et l'anisotropie des éléments fabriqués 3D à partir de ces matériaux. Ces objectifs ont été explorés à travers cinq publications scientifiques, composant les cinq chapitres de cette thèse.

Dans notre première contribution, nous avons synthétisé des sols de phosphate d'aluminium photopolymérisables, qui ont été polymérisés pour aboutir à des matériaux hybrides organiques-inorganiques (OIH) composés de chaînes de poly (méthacrylate de 2-hydroxyéthyle) avec des groupes de phosphate d'aluminium liés de manière covalente au squelette polymère. Ces unités inorganiques fournissent de nombreux agents de réticulation, résultant en une structure inorganique/organique hautement interconnectée et imbriquée. Les matériaux OIH étaient optiquement transparents entre 420 nm et 1100 nm, cependant, ces matériaux présentaient une faible transmission dans la région du proche infrarouge (NIR) en raison de la forte teneur en matières organiques de ces matrices.

Dans une deuxième contribution, nous avons modifié la voie de synthèse pour obtenir des matériaux OIH aluminium-phosphate-silicate avec une concentration en masse inorganique plus élevée et une transmittance améliorée dans le NIR. Nous avons étudié en profondeur la structure de

ces matériaux avec la RMN à l'état solide et observé que le réseau inorganique est formé d'unités d'aluminium-phosphate interconnectées par des chaînes de silicate. L'environnement chimique des sites de phosphate et d'aluminate pourrait être réglé en fonction du rapport aluminium sur phosphore, permettant à la structure d'être adaptée afin d'améliorer la capacité d'accueil des ions lanthanides de ces matériaux. Ces caractéristiques structurelles présentent ces matériaux comme des candidats potentiels pour immobiliser les ions lanthanides pour développer des composants optiques actifs.

Dans une troisième contribution, nous avons développé et testé un modèle mathématique décrivant le profil d'exposition produit par l'imprimante utilisée dans ce travail, nous permettant de modéliser l'interaction laser-résine dans cet équipement, et de corréler les paramètres d'impression mesurés pour notre matériau avec ceux des systèmes FA commerciales. De plus, nous avons identifié que ce système d'impression peut, théoriquement, imprimer plus rapidement par rapport aux plateformes commerciales dans des conditions spécifiques de diamètre de faisceau et de chevauchement entre les impulsions.

Dans une quatrième contribution, nous avons exploré la fabrication additive des résines aluminium-phosphate-silicate. L'évolution des paramètres d'impression 3D de ces matériaux (énergie critique et profondeur de pénétration), et de la cinétique de photopolymérisation avec l'intensité lumineuse et la concentration en silicate a été étudiée. Ces résultats indiquent le déplacement de la conversion critique vers un degré de polymérisation plus élevé à mesure que la concentration de silicate augmente, ce qui était associé à une tendance plus élevée à la cyclisation. Ces résultats ont été utilisés pour valider un modèle photochimique publié dans la littérature décrivant l'interaction laser-résine dans les systèmes VPP, élucidant le lien entre l'énergie critique et la cinétique de photopolymérisation.

Dans notre dernière contribution, nous avons étudié la distribution de l'indice de réfraction et la présence d'anisotropies optiques dans les lignes imprimées en 3D. Nous avons identifié que les pièces imprimées en 3D sont optiquement homogènes, malgré la présence d'un gradient de degré de polymérisation associé à la pénétration du laser dans la résine et au profil du faisceau. Des anisotropies optiques ont été identifiées et des mesures micro-Raman polarisées indiquent que la biréfringence provient de la contrainte de cisaillement perpendiculaire à la direction de balayage due à l'afflux de monomère vers le point de polymérisation.

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LIST OF ABBREVIATIONS

ABS	<i>Acrylonitrile Butadiene Styrene</i>
ACAC	<i>Acetyl Acetate</i>
AFM	<i>Atomic Force Microscopy</i>
AIBN	<i>Azobisisobutyronitrile</i>
AJ	<i>Adhesive Joining</i>
AM	<i>Additive Manufacturing</i>
ATR	<i>Attenuated Total Reflectance</i>
BAPO	<i>Phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide</i>
BJT	<i>Binder Jetting</i>
BSE	<i>Backscattered Electrons</i>
CAD	<i>Computer-Aided-Design</i>
CE	<i>Continuous Exposure</i>
CLIP	<i>Continuous Liquid Interface Production</i>
CN	<i>Coordination Number</i>
CP	<i>Cross-Polarization</i>
CPMAS	<i>Cross-Polarization Magical Angle Spinning</i>
CQ	<i>Quadrupolar coupling</i>
CRB	<i>Chemical Reaction Bonding</i>
CRC	<i>Chemical Reaction Consolidation</i>
CW	<i>Continuous Wave</i>
DDM	<i>Direct Digital Manufacturing</i>
DED	<i>Direct Energy Deposition</i>
DIW	<i>Direct Ink Writing</i>
DLP	<i>Digital Light Processing</i>
DMD	<i>Digital Micromirror Device</i>
3DP	<i>Three-Dimensional Printing</i>
DQ	<i>Double Quantum</i>
DTG	<i>Differential Thermogravimetric Analysis</i>
EB	<i>Electron Beam</i>
EOF	<i>Exposure Overlap Factor</i>

EPMA	<i>Electron Probe Microanalyzer</i>
EXSY	<i>Exchange Spectroscopy</i>
FA	<i>Fabrication Additif</i>
FDM	<i>Filament Deposition Modelling</i>
FM	<i>Formative Manufacturing</i>
FTIR	<i>Fourier Transform Infrared Spectroscopy</i>
HDA	<i>1, 6-hexanediol diacrylate</i>
HEMA	<i>2-hydroxyethyl methacrylate</i>
HETCOR	<i>Heteronuclear Correlation</i>
HOI	<i>Híbrido Organico-Inorganico</i>
HEMA-P	<i>hydroxyethyl methacrylate-phosphoric acid ester</i>
IE	<i>Intermittent Exposure</i>
IPN	<i>Interpenetrating Polymeric Network</i>
IR	<i>Infrared</i>
LAM	<i>Laser Additive Manufacturing</i>
LB	<i>Laser Beam</i>
LCD	<i>Liquid crystal display</i>
LED	<i>Light Emitting Diode</i>
MA	<i>Manufatura Aditiva</i>
MAEAA or MAEEA	<i>2-(Methacryloyloxy)ethyl acetoacetate</i>
MAS	<i>Magical Angle Spinning</i>
MEV	<i>Microscopia Eletrônica de Varredura</i>
MEX	<i>Material Extrusion</i>
MJT	<i>Material Jetting</i>
MOF	<i>Metal-Organic Framework</i>
MPP	<i>Multiphoton photopolymerization</i>
MPTMS or TMSPM or MTMS	<i>3-(trimethoxysilyl)propyl methacrylate</i>
ND	<i>Neutral Density</i>
NIR	<i>Near Infrared Region</i>
NMR	<i>Nuclear Magnetic Resonance</i>
OIH	<i>Organic Inorganic Hybrid</i>
ORMOCER	<i>Organically Modified Ceramic</i>

ORMOSIL	<i>Organically Modified Silane</i>
PBF	<i>Power Bed Fusion</i>
PC	<i>Polycarbonate</i>
PETA	<i>Pentaerythritol Tetra Acrylate</i>
PHEMA	<i>Poly Hydroxyethyl Methacrylate</i>
PLA	<i>Poly Lactic Acid</i>
PLC	<i>Poly Caprolactam</i>
PMMA	<i>Poly Methyl Methacrylate</i>
REDOR	<i>Rotational Echo Double Resonance</i>
RMN	<i>Ressonância Magnética Nuclear</i>
SEM	<i>Scanning Electron Microscopy</i>
SERS	<i>Surface Enhanced Raman Scattering</i>
SHL	<i>Sheet Lamination</i>
SLA	<i>Stereolithography</i>
SM	<i>Subtractive Manufacturing</i>
SOQE	<i>Second Order Quadrupolar Effect</i>
SQ	<i>Single Quantum</i>
TGA	<i>Thermogravimetric Analysis</i>
TMS	<i>Tetramethyl Silane</i>
TPO	<i>Diphenyl(2, 4, 6- trimethyl benzoyl)phosphine oxide</i>
TQMAS	<i>Triple Quantum Magic Angle Spinning</i>
TRB	<i>Thermal Reaction Bonding</i>
UC	<i>Ultrasonic Consolidation</i>
UV	<i>Ultraviolet</i>
UVL	<i>Ultraviolet Laser</i>
UVM	<i>Ultraviolet Mask</i>
VIS	<i>Visible</i>
VPP	<i>Vat Photopolymerization</i>
WAMM	<i>Wire and Arc Additive Manufacturing</i>
WDS	<i>Wavelength Dispersive Spectroscopy</i>

To my family, friends, and colleagues, with whom I shared, even for a brief moment, this tortuous and long path. I am grateful for their love and support.

ACKNOWLEDGEMENTS

The Ph.D. is quite a long path that is only possible, directly, or indirectly, by the people we meet on the way. I would like to use this space to remember and express my gratitude to all these people.

Normally I would start this section by thanking my supervisors, however I find it fitting to start by expressing my thanks to Julie Frechette. She is the only reason I managed to go to Canada as a cotutelle student. It was easily a more than one-year process of emails and correspondence going back and forth between the two universities that she had to manage. Thank you.

Now, I would like to thank Prof. Younes Messaddeq, and Prof. Tigran Galstian for their supervision, expertise, and enthusiasm. My Ph.D. was only possible because they gave me the opportunity to work, and most important, learn with them. Their guidance and support were essential. For similar reasons, I must also thank Prof. Marcelo Nalin, and Prof. Edgar Dutra Zanotto who were the pillars of my formation and gave me multiple opportunities that led me all the way here.

I have absolutely no way of expressing how grateful I am to Silvia Santagneli. She was the one who advised me during my stay in Brazil, and I can definitely say that Silvia's contribution towards this Ph.D. project could not be replaced. Her wide expertise in solid-state NMR, her patience to teach, and her supervision guided me through more than half of this thesis.

I must also express my gratitude towards my co-supervisor in Canada, Ph.D. Sandra Helena Messaddeq, for her insightful comments, constructive criticism, and helpful suggestions. Her feedback has greatly contributed to the quality of my research concerning the additive manufacturing.

I would like to thank the staff and faculty of Instituto de Quimica de Araraquara (UNESP) and COPL (Universite Laval), with special emphasis to the technicians Rafael Domeneguetti, Sergio Scarpari and Patrick Larochelle for their support and resources that have been instrumental in enabling me to carry out this research. Their assistance has been essential in navigating the various stages of the research process. Similarly, I must acknowledge the administrative staff at both universities, especially Wenia, Robson, Cintia, Michelle, Caroline, and David Helie for their support.

I am grateful as well to Prof Hellmut Eckert, Prof. Marcos de Oliveira Junior, and Ph.D. Shane Pawsey who collaborated in the publications integrating this thesis. Their insights, expertise, suggestions, and criticism were unvaluable for the quality of this thesis, as well my personal and professional development.

I would like to express my gratitude towards the whole Photonic Materials Group in Araraquara with special mention to Prof. Sidney Ribeiro, Prof. Willy Glen Santos, Prof. Elias Paiva Ferreira Neto, Prof. Danilo Manzani and Prof. Edson Percoraro for their scientific contributions. Similarly, I thank my friends from UNESP, Natalia Medeiros, Bruno Ekawa, Daniela Vassalo, Juliana Resges, Leonardo Albino, Leonardo Marchiori, Nina, Thais, Bia, Lia, Lais Galvao, Adriane Cherpinski and York for their support, encouragement, and great time together.

I would like to express my gratitude towards the whole Younes Messaddeq Lab in Universite Laval for their contribution, suggestions, and support for my thesis with special mention to Wagner Correr, and Prof. Ali Riaz. Similarly, I thank my friends from Universite Laval Hasnaa, Samar, Can, Alizee, Anees, Ishfaq, Rizan, Ismail, Nathaly, Iago, Rodrigo, Orisson, Victor, Alice, Mehran, Thomas, Brice, Simon, Theo, Antonin, and my friends from COPL, which is a pretty long list. In this regard, I must acknowledge all my Iranian friends and their fight for a better future in their country. Women, life, freedom.

I am also grateful to my family and friends for their unwavering support throughout my academic journey. Their love, support, and understanding have been crucial in helping me stay motivated and focused. Thank you Nkosi, Leleo, Gabi, Trop, Pita, Mari, my father, mother, and brother, and Halili, my love.

Lastly, this thesis was only possible thanks to the financial support of FAPESP (2018/06426-3, 2019/24367-7, 2015/ 22828-6, and 18/ 24735-3), and CNPQ (141186/2018-6).

Thank you all for your support, encouragement, and contributions. I could not have completed this thesis without your help and guidance.

FOREWORD

This thesis manuscript was based on four published manuscripts in peer-reviewed journals plus one unpublished work. Gabriel T. Tayama is the first author in three of them, and second author in the remaining one. A list of these articles is provided below, with details of submission and publication dates. Further information on the contribution of each co-author, and the alterations from the original manuscript to the version presented in this thesis manuscript are also provided.

Title: Understanding the Microstructure Connectivity in Photopolymerizable Aluminum-Phosphate-Silicate Sol–Gel Hybrid Materials for Additive Manufacturing

Authors: G. T. Tayama, S. H. Santagneli, M. de Oliveira Junior, and Y. Messaddeq,

Journal: Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.2c08027.

Status: Submitted on November 15th, 2022. Published on January 19th, 2023.

Co-author Contributions: Synthesis of the materials, sample preparation, and all characterizations, except solid-state NMR, were executed by Gabriel Tayama. ²⁹Si, ²⁷Al, and ³¹P uni- and bidimensional solid-state NMR experiments were performed by Ph.D. Silvia Santagneli. ¹H, and ¹³C uni- and bidimensional solid-state NMR experiments were performed by Prof. Marcos Junior. Data interpretation was performed by Gabriel Tayama, Ph.D. Silvia Santagneli and Prof. Marcos Junior. The manuscript was prepared by Gabriel Tayama, and reviewed, edited, and completed by Ph.D. Silvia Santagneli and Prof. Marcos Junior. Prof. Younes Messaddeq supervised all the steps during the execution of this work.

Description of alterations: Formatting (font and line spacing) were adjusted to match the requirements of FESP. The figure numbering was adjusted to match the numbering of other figures presented along the thesis document. An abstract in French and in Portuguese was added.

Title: Preparation and Structural Characterization of New Photopolymerizable Transparent Aluminum-Phosphate Hybrid Materials as Resins for 3D Printing

Authors: G. T. Tayama, S. H. Santagneli, H. Eckert, S. Pawsey, and Y. Messaddeq

Journal: Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.0c08289

Status: Submitted on September 10th, 2020. Published on November 10th, 2020.

Co-author Contributions: Synthesis of the materials, sample preparation, and all characterizations, except solid-state NMR, were executed by Gabriel Tayama. ²⁹Si, ²⁷Al, and ³¹P uni- and bidimensional solid-state NMR experiments were performed by Ph.D. Silvia Santagneli. ¹H, and ¹³C uni- and bidimensional solid-state NMR experiments were performed by Ph.D. Shane Pawsey. Data interpretation was performed by Gabriel Tayama, Ph.D. Silvia Santagneli, Ph.D. Shane Pawsey, and Prof. Hellmut Eckert. The manuscript was prepared by Gabriel Tayama, and reviewed, edited, and completed by Ph.D. Silvia Santagneli, Ph.D. Shane Pawsey and Prof. Hellmut Eckert. Prof. Younes Messaddeq supervised all the steps during the execution of this work.

Description of alterations: Formatting (font and line spacing) were adjusted to match the requirements of FESP. The figure numbering was adjusted to match the numbering of other figures presented along the thesis document. An abstract in French and in Portuguese was added.

Title: Process modeling of laser scanning vat-photopolymerization operating under intermittent exposure conditions

Authors: M. Posternak, G. T. Tayama, S. H. Messaddeq, and Y. Messaddeq,

Journal: Additive Manufacturing

DOI: 10.1016/j.addma.2022.103234

Status: Submitted on April 18th, 2022. Published on October 14th, 2022.

Co-author Contributions: Synthesis of the materials, sample preparation, and all characterizations were executed by Mykola Posternak. Data interpretation and the mathematical modelling was performed by Gabriel Tayama. The manuscript was prepared by Gabriel Tayama, and reviewed, edited, and completed by Ph.D. Sandra Messaddeq. Prof. Younes Messaddeq supervised all the steps during the execution of this work.

Description of alterations: Formatting (font and line spacing) were adjusted to match the requirements of FESP. The figure numbering was adjusted to match the numbering of other figures presented along the thesis document. An abstract in French and in Portuguese was added. Bibliographic references were adjusted to match the ACS (American Chemical Society) citation style.

Title: Correlation Between Critical Energy, Penetration Depth, and Photopolymerization Kinetics in Aluminum-Phosphate-Silicate Hybrid Materials for Vat-Photopolymerization

Authors: G. T. Tayama, S. H. Messaddeq, S. H. Santagneli, and Y. Messaddeq

Journal: Macromolecules

DOI: 10.1021/acs.macromol.3c00363

Status: Submitted on February 27th, 2023. Accepted on May 12th, 2023.

Co-author Contributions: Synthesis of the materials, sample preparation, and all characterizations were executed by Gabriel Tayama, except solid-state NMR (S. H. Santagneli). Data analysis, and interpretation was executed by Gabriel Tayama. The manuscript was prepared by Gabriel Tayama, and reviewed, edited, and completed by Ph.D. Sandra Messaddeq, Ph.D. Silvia Santagneli. Prof. Younes Messaddeq supervised all the steps during the execution of this work.

Description of alterations: Formatting (font and line spacing) were adjusted to match the requirements of FESP. The figure numbering was adjusted to match the numbering of other figures presented along the thesis document. An abstract in French and in Portuguese was added.

Title: Refractive Index Distribution and Optical Anisotropies in Additive Manufactured Materials

Authors: G. T. Tayama, S. H. Messaddeq, Tigran Galstian, and Y. Messaddeq

Status: Results to be published.

Co-author Contributions: Synthesis of the materials, sample preparation, and all characterizations were executed by Gabriel Tayama. Data analysis, and interpretation was executed by Gabriel Tayama. The manuscript was prepared by Gabriel Tayama, and reviewed, edited, and completed by Ph.D. Sandra Messaddeq, Prof. Tigran Galstian. Prof. Younes Messaddeq, and Prof. Tigran Galstian supervised all the steps during the execution of this work.

Description of alterations: Formatting (font and line spacing) were adjusted to match the requirements of FESP. The figure numbering was adjusted to match the numbering of other figures presented along the thesis document. An abstract in French and in Portuguese was added.

INTRODUCTION

Three-dimensional printing or additive manufacturing (AM) refers to a family of different techniques sharing a layer-by-layer manufacturing approach. Because of its features, AM allow the fabrication of complex structures with fixed processing time and costs, and simplified process planning, which is ideal for the small-scale production of high customizable products [1]. There are extensive reviews on literature on how additive manufacturing technologies are promising for a wide range of applications [2]–[4].

AM is a promising technology for photonic applications which has received great attention in the last decade as a method to circumvent the limitations of traditional manufacturing methods, which could enable a new generation of integrated optical devices. AM technologies for photonics requires high resolution ($<10\text{ }\mu\text{m}$) and high surface finishing quality [5], which are conditions met by few AM technologies. The vat-photopolymerization (VPP) family of techniques is one of the few who meet such requirements, and although there are numerous examples in literature concerning the use of VPP in photonics, there are few fundamental investigations on the optical quality of produced parts, especially when it concerns optical homogeneity and anisotropies, since AM is a fundamentally anisotropic process.

The availability of materials compatible with VPP techniques is one of the main issues preventing more expressive application of VPP into the manufacturing of optical devices. VPP construct objects by inducing the selective photopolymerization of a resin to form each layer, therefore this technique is constrained to methacrylate and epoxy-based polymers. The organic nature of polymers restricts the optical applications of objects manufactured by AM to the visible and the terahertz regimes of the electromagnetic spectrum [6], [7]. In recent years, there has been intense research to enable the AM of inorganic glasses via VPP, which is a staple optical material for both active and passive optical devices. The main drawback, however, is that all approaches available require thermal treatment at high temperatures, hindering the construction of integrated electro-optical devices. In this context, the use of organic-inorganic hybrid (OIH) materials with VPP has arisen as an alternative to polymeric materials and inorganic glasses, since their optical properties can be tuned to meet the transmission requirements for active and passive optical devices operating from UV (ultraviolet) to NIR (near-infrared) spectrum [5], [8], [9]. They are not widely explored in photonics as glasses, however they are

excellent candidates for integrated active and passive photonic structures, since they do not require thermal treatments[5], [8], [10]–[12]

The hybrid sol-gel route has emerged in the last 3 years as a convenient chemical route to obtain transparent OIH materials processable through VPP. This chemical route employs chemical precursors capable of forming inorganic bonds through condensation reactions at mild processing conditions, with pendant photopolymerizable groups for the VPP process [13]. Alternative synthesis routes for OIH materials are not innately compatible for VPP as the hybrid sol-gel route, and often suffer from phase segregation, yielding opaque materials [14]–[16]. Controlling the hydrolysis and condensation reactions are a fundamental step in this chemical route because it allows the organic and inorganic connectivity to be tailored and avoid phase segregation, resulting in a transparent material. So far, this chemical route has successfully allowed the printing of silicate-based OIHs with good optical quality, which have been explored in the fabrication of passive optical structures, such as waveguides [17], [18]. However, these matrices are bad candidates for the development of active optical devices, because of their poor solubility of lanthanide ions, requiring either thermal treatment at high temperature or additional strategies to introduce the lanthanide ions in the structure. Thus, there is the need for OIH materials which are inherently compatible with the chemistry of lanthanides for the fabrication of active optical devices via VPP.

In this regard, aluminum-phosphate (AIP) OIH materials are promising candidates for the fabrication of active optical devices. The chemistry of aluminum-phosphate shows a remarkable solubility for lanthanide ions, which prevents clustering and concentration quenching in photoluminescence[19], [20]. As a matter of fact, AIP inorganic glasses are widely used in telecommunications as signal amplifiers and fiber lasers. Despite these characteristics, little is reported in literature about AIP OIH materials obtained through the hybrid sol-gel route. The AIP sol-gel chemistry is challenging compared to the well-established silicate sol-gel chemistry. For instance, there is no convenient phosphate precursor for sol-gel chemistry, being either too reactive or unreactive [21]. Aluminum precursors in sol-gel chemistry are too reactive and require special complexing agents to reduce their reactivity [22], [23]. When aluminum and phosphate precursors are combined, their reaction results in precipitation or gelation, hindering the materials transparency. To date, there is little information on the synthesis of transparent and photopolymerizable AIP OIH materials.

In this work, we developed AIP OIH materials by the hybrid sol-bel approach. These materials are stable resins that can undergo photopolymerization, and be processed by VPP, to result in transparent hybrid materials. These materials' structure and properties were characterized in-depth using a different technique. Furthermore, we modelled the exposure profile of a custom-made VPP setup, which was further employed in the additive manufacturing of these materials. Lastly, we analyzed the optical properties of the additive manufactured elements to assess their optical homogeneity and the presence of anisotropies. A bibliography review concerning the main points related to this project, that is, additive manufacturing and its application in photonics, the technicalities of VPP process, and the hybrid sol-gel approach, are presented below.

Additive manufacturing (AM)

a. Definition and history

Additive manufacturing (AM), also known as three-dimensional printing (3DP), is an umbrella term encompassing different manufacturing techniques sharing the same layer-by-layer approach for fabrication based on a digital model, as shown in **Figure 1** [24]. Historically, the first AM technologies date back to 1800s, however it is widely recognized that the modern starting point of AM technologies was the patents filed in 1984s by Charles Hull, which started to be commercialized by the company 3D Systems established in 1986 [4]. In its early days, AM was better known as rapid prototyping (RP) because it was originally designed to allow the fast fabrication of prototypes and physical models required for product design. The evolution of AM as a proper manufacturing method was only possible due to the technological advances in printing, laser, and numerical control technologies, computer graphics, computer-aided design (CAD), and materials availability [4], [24]. AM platforms were able to print faster, cheaper, more accurate, and with a wider range of materials, leading AM to be slowly incorporated into the production chain of some industrial sectors. The field steadily grew with the application of new patents and foundation of new companies, stimulating research and development [4]. However, AM technologies were still expensive, because of intellectual property, and the low availability of personnel with know-how restricted widespread adoption of AM by the industry.

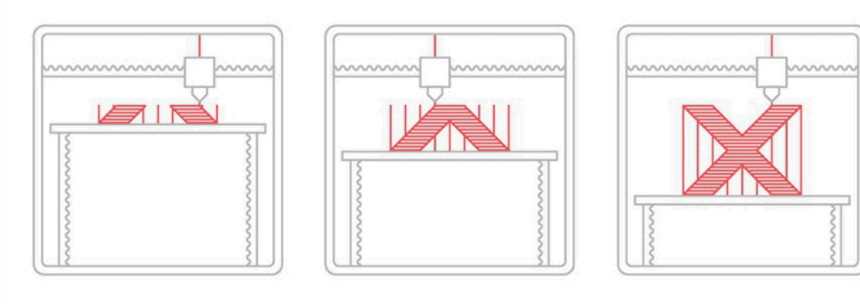


Figure 1. Layer-by-layer principle of a generic additive manufacturing method [25].

The boom of AM occurred in the 2000s, with 2007 being considered a milestone due to the expiration of many AM related patents. Numerous companies appeared and the domestic market became a hotspot, lowering the cost of AM platforms, resulting in a leap from 60 3D printers in 2007 to 23000 in 2011 marketed in the domestic market[4]. The easy access to AM platforms allowed different industrial sectors and research institutes to explore the applicability of AM in their fields. This is evident if we analyze the evolution of publications and patents in the last years as shown by the web of Science database and Espacenet ("additive manufact*" OR "3D print*" OR "rapid protot*"), and compiled in **Figure 2**. Today, the term DDM (*Direct digital manufacturing*) is already used, referring to the additive manufacturing process where the final product is entirely manufactured by AM techniques.

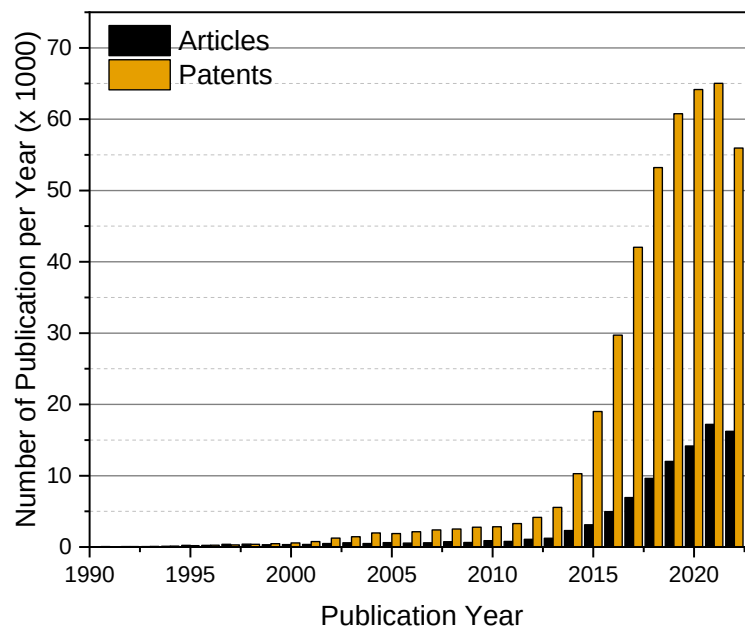


Figure 2. Research string ("additive manufact*" OR "3D print*" OR "rapid protot*") in Espacenet and Web of Science (Web of Science Core Collection database)

b. The AM process

A generic AM process is composed by four major steps, as illustrated in **Figure 3**. The first step consists in obtaining a digital tridimensional representation of the desired geometry's or object's surface. This is accomplished with CAD (*computer-aided design*) softwares, such as SketchUp®, and SolidWorks®, or though imaging techniques such as laser scanning and tomography. The design is saved as a STL file, which is the standard file format used by AM systems. This format describes the surface of an object as a collection of triangles in cartesian coordinates. The second step comprehends the manipulation of the STL file and slicing, which is done in a software provided by the own AM equipment manufacturer, or directly in the AM equipment. Adjustments such as position, orientation and size are made, and the object is sliced in numerous cross-section layers representing the printing instructions for each layer. The third step is the transference of the file to the equipment and the adjustments of the printing settings by the operator. The printing settings are related to the building parameters according to the type of AM equipment and it physical-chemical process responsible for the fabrication. The printing process starts, which is fully automated, and does not require any supervision. Once finished, the object is removed. The fourth step is post processing, which will depend on the application, which could include polishing, thermal treatment, rinsing and drying, depending on the AM technique.

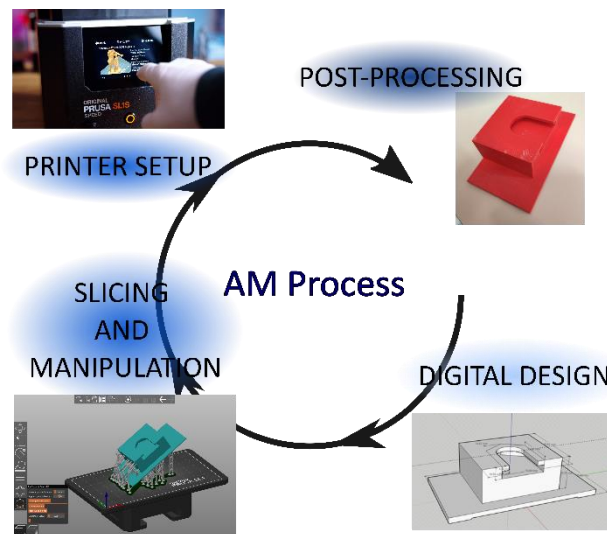


Figure 3. The main steps of a generic AM process.

c. AM and Industry

The importance of AM in the industry arises from the intrinsic limitations associated by traditional manufacturing, which encompasses formative (FM) and subtractive (SM) manufacturing methods. In FM methods, the final shape of the object is obtained by casting, blowing, or plastic deformation strategies, while in SM this is achieved by removing material from a raw workpiece[26]. A common problem with both methods is geometry constraints, making it challenging and requiring a large number of productive steps (and time) to achieve certain shapes. FM is an appropriate manufacturing method for mass produced goods, due to the high acquisition cost of the equipment and subsequent modifications. SM, on the other hand, is specially suited for small scale production of goods with high accuracy, however it suffers from low throughput, high material waste, and high cost. Ultimately, we lack a manufacturing method for fast and small-scale production of complex articles, at low cost and material consumption, which are the features of AM [27].

These limitations are a problem in face of Industry 4.0 concept, whose ultimate goal is to achieve a more efficient (material and energy consumption) fabrication process with real time feedback of custom-made products [28]–[30]. Industry 4.0 is centered in the real-time intercommunication between management and autonomous industrial equipment, so that production and decisions are decentralized. Many technologies such as artificial intelligence, robotics, and Internet of Things have been presented as enabler towards the concept. Not surprisingly, AM is also considered an enabler technology, because it solves the aforementioned problems, and has an innate integration with digital systems. Another advantage of AM is the fact that the final part is directly correlated to its digital drawing, allowing the part performance to be further analyzed using engineering softwares to assess the feasibility of the project, speeding up optimization interactions during fabrication process [24].

There is still a lot of research on the implementation of AM process in the context of Industry 4.0, since the concept is still under development. Nonetheless, AM already occupies a strategic position in the production chain of different industrial segments, especially for developed countries, since mass production lines have migrated to developing countries. [31]. Essentially, AM enables the fabrication of high aggregated value products, and is regarded as a disruptive technology regarding the design, production and marketing of new products. There is great enthusiasm around its potential, and it has been envisioned as the beginning of another industrial revolution [24]. It represented a USD 13.84

billion in 2021, with projections of a 20% per year growth, expecting to reach a USD 76.12 billion by 2030, forcing industry to rethink its processes, production chain and organizational structure [32].

The most successful case of AM application in industry is the fabrication of hearing aids. About 97% of hearing aids are fabricated by 3D printing, reducing from 40% to 10% the rate of return due to poor fitting at lower price [25]. Many industrial segments and companies are integrating AM into their production chain, such as aerospace, automotive [33], medical and dental, tooling, health and biosciences applications, education [34], drug release systems [35], food industry[36], [37] just to cite a few.

d. Families of AM techniques

There is a great variety of AM technologies available, which led to their grouping and categorizing based in different criteria, such as the type of material printed. The most adopted classification was initially introduced by the ASTM F2792-12a [38], later becoming ISO/ASTM 52900:2021 [39], based on the configuration of the equipment used and the physical-chemical process involved in the layer formation, grouping into seven process categories. A concise description of each category, its features, and additional information on the most representative techniques for each process category is presented below. The objective of this section is to brief the reader into the type of materials, printing resolution and surface finishing achievable by each process category in order to understand why some techniques are far more interesting for photonic applications compared to other. Reference literature is provided for additional information for each one of these techniques and categories.

- Binder jetting (BJT) typically works in a two-step process. First a layer of powdered material is spread in the build chamber, then, a liquid binding agent is selectively deposited on top of the powdered materials to form one of the layers. The process repeats multiple times until all layers are printed. **Figure 4** shows the typical scheme of a BJT AM system [40]. Sand, metals, and ceramics are the most common materials for BJT, with some limited work on plastics. BJT of sand is typically used for fabricating dies for metal casting. In the case of metals and ceramics BJT, additional thermal treatment eliminates the binder and allows sintering to consolidate the metallic or ceramic part [25]. The technique is low cost, with feasible layer thickness as low as 30 μm . The technique is also suitable for large objects (500 mm), however post processing is required to improve surface finishing and the high porosity. It displays high printing speeds (up to 200 $\text{cm}^3.\text{min}^{-1}$) [40].

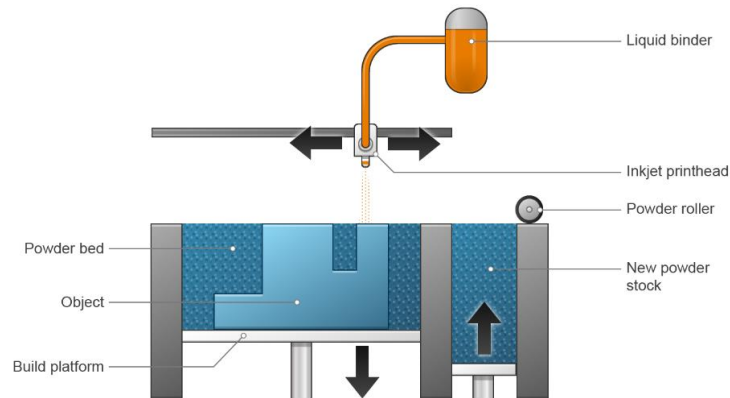


Figure 4. Typical scheme of a BJT additive manufacturing system. Extracted from <https://make.3dexperience.3ds.com/processes/material-jetting> on 10th of March 2023.

- Directed energy deposition (DED): a material (mostly metals), in the form of a filament or powder, is deposited and melted simultaneously by means of a concentrated source of thermal energy, such as a laser beam (-LB), electron beam (-EB) or electric arc (-Arc), following the ISO/ASTM 52900:2021 nomenclature [39]. DED techniques are grouped according to the type of feedstock employed (powder or filament) and the thermal source[41]. A typical DED AM system is presented in **Figure 5**. Resolution in the XY and in the Z axis depends on the specifications of each equipment, however the minimum values reported in literature are of 380 and 200 μm , respectively [41]. The technique suffers from poor surface finishing, with typical surface roughness higher than 25 μm .

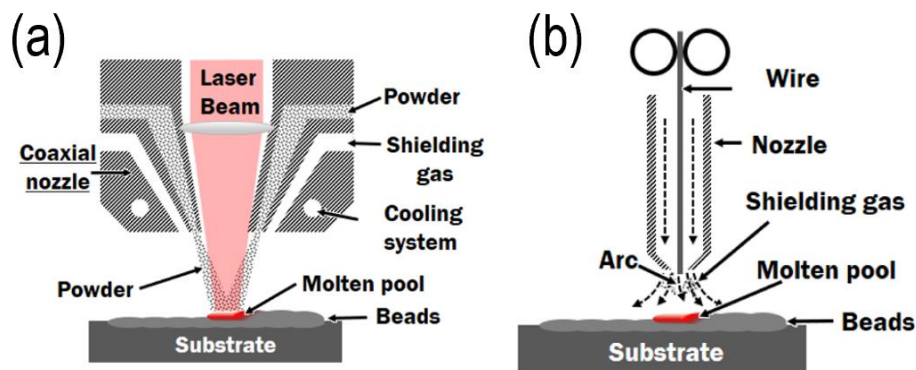


Figure 5. Typical schemes of a DED additive manufacturing system for a LAM (Laser Additive Manufacturing) in (a) and a WAMM (Wire and Arc Additive Manufacturing) in (b) [41].

- Material extrusion (MEX) is the most representative AM technology, being widely accessible for all commercial segments, ranging from a hobbyist to industrial production. These processes rely on continuously extruding the printing material through a nozzle, allowing the selective depositions of the

material on the building plate[24]. The main difference between the different AM techniques integrating MEX is the method for bonding the material after extrusion, which can be through a chemical reaction (-CRB) or a thermal reaction (-TRB), following the ISO/ASTM 52900:2021 nomenclature [39]. A typical MEX AM system is showed in **Figure 6**. The most well-known MEX technique is the fused deposition modelling (FDM), where a polymeric filaments is liquified and solidified by controlling the temperature. Direct Ink Writing (DIW) is another well-known method, where the feedstock material is either a liquid or gel, which solidifies upon light exposure, temperature control or low shear rate. MEX is typically used for printing polymers such as acrylonitrile-butadiene-styrene (ABS), poly caprolactone (PLC), polycarbonate (PC), and poly lactic acid (PLA) [24], [25]. Printing resolution is defined by the nozzle diameter, which is around 100 μm for most commercial equipment. MEX technologies are quite inexpensive, being able to print large volumes of material (1 m^3) but have limited dimensional accuracy and poor surface finish[42].

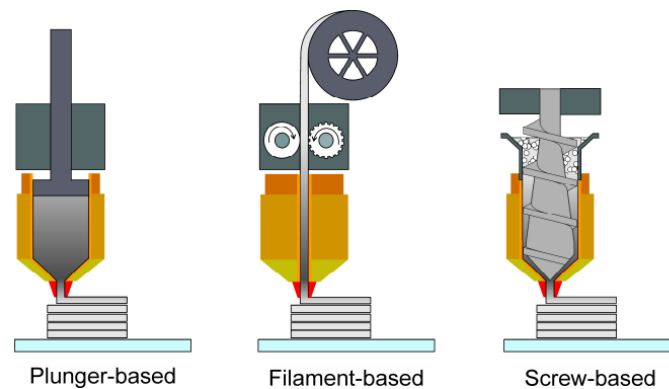


Figure 6. Typical scheme of a MEX additive manufacturing system employing different methods of extrusion. [43]

- Power bed fusion (PBF) is based on the selective fusion/sintering of particulate matter using a thermal source, typically a laser beam (-LB), electron beam (-EB), or infrared light (-IrL), following the ISO/ASTM 52900:2021 nomenclature [39]. In PBF, a layer of particulate raw material is deposited in the printing chamber, which is then scanned with the thermal source, forming that layer. A second layer of particulate material is then deposited, and the process repeats. A typical PBF AM system is presented in **Figure 7**. PBF is a widespread AM technology due to its low cost/part quality relationship compared to other AM process[24]. Furthermore, PBF is compatible with a wide range of materials, such as metals, ceramics, glasses, and polymers, and unused raw materials during one printing process can be easily reused [44]. The printing resolution of PBF process depends on the type of

material, the physical or chemical process associated, and the heat source. Typically, resolution on the order of 100 μm is easily achievable, however the printed parts have high porosity [24].

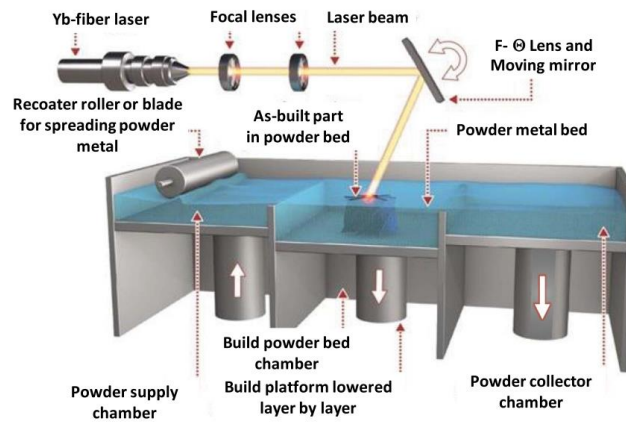


Figure 7. Typical scheme of a PBF additive manufacturing system. [45]

- Sheet lamination (SHL): process of building an object from the joining of plates of the desired material by means of an adhesive joining (-AJ) or ultrasonic consolidation (-UC), following the ISO/ASTM 52900:2021 nomenclature [39]. There is little literature on this AM category, and the technology is still in development. Most companies which were formed to commercialize SHL techniques have gone out of business or abandoned this technology. **Figure 8** shows a typical SHL AM system.

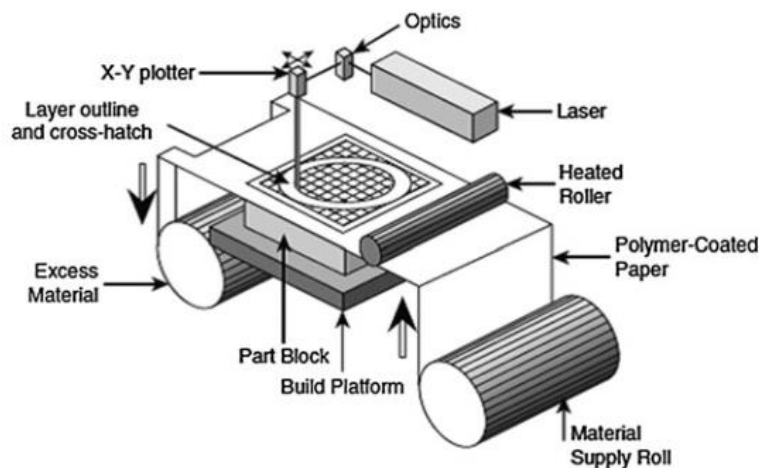


Figure 8. Typical scheme of a SHL-AJ additive manufacturing system. [24]

- Material jetting (MJT) works by selectively depositing droplets of raw material to form a layer, in a similar fashion as paper inkjet printer, followed by material consolidation, which can be achieved

by curing under ultraviolet light (-UV), by a chemical reaction (-CRC) or thermal reaction (-TRB), following the ISO/ASTM 52900:2021 nomenclature [39]. The materials employed are typically photopolymers, which are exposed to UV light once each layer is printed. A typical MJT AM system is presented in **Figure 9**. MJT is known for its high-quality printing, being able to print thin walls with very low staircase effect (visible layers). The technique allows resolution in Z axis as low as 16 μm [46]. In addition to polymers, developments for printing metals using this technique are already commercialized. This process has excellent surface finish, but its cost is high, and the materials development can be quite complicated due to strict rheological properties required for droplet formation [47].

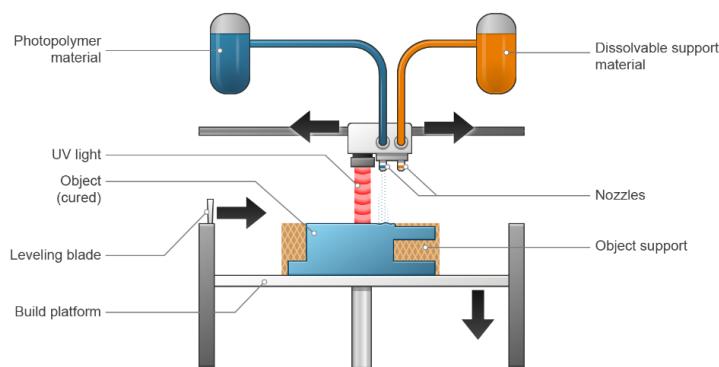


Figure 9. Typical scheme of a MJT-UV additive manufacturing system. Extracted from <https://make.3dexperience.3ds.com/processes/material-jetting> on 10th of March 2023.

- Vat photopolymerization (VPP) refers to a family of 3DP technologies based on the selective photopolymerization of a resin through localized light exposure (typically UV light) [48], [49]. The light exposure can be achieved by means of a guided ultraviolet laser (-UVL), ultraviolet light passing through a mask (-UVM) or by exposure to light emitting diodes (-LED), following the ISO/ASTM 52900:2021 nomenclature [39]. There are different VPP setups, however the most common is the stereolithography (SLA), which employs a UV laser as a light source. Examples of VPP AM systems are presented in **Figure 10**. These techniques excel in spatial resolution, printing time and surface finishing compared to other 3DP technologies, allowing the fabrication of objects with numerous fine features/structures [27], [50]. For instance, most commercial platforms are able to print features down to 25 μm , meanwhile high spec commercial printers and multiphoton polymerization setups can reach 10 μm and 200 nm resolution [24], [25], [27], respectively. Only methacrylate and epoxy-based polymers are compatible with VPP approach, however in the last years there has been considerable effort to print ceramics and glasses as well. It is one of the most dimensionally accurate AM techniques,

with great surface finish and ability to print highly detailed structures [24], [25]. Because of these characteristics, vat photopolymerization techniques are the most interesting for application in photonics, since surface quality and printing resolution are key parameters for such field[5].

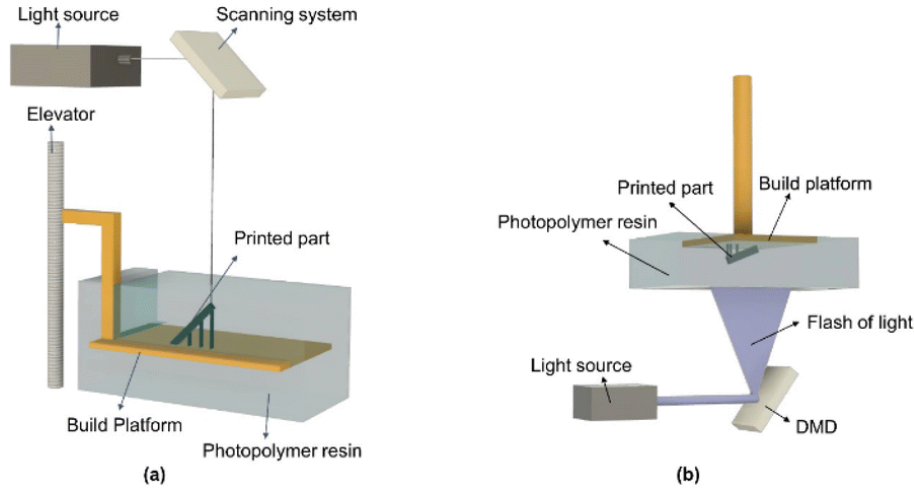


Figure 10. Typical scheme of VPP-UV and VPP-UVM additive manufacturing system in (a) and (b), respectively. [51]

e. AM for photonic applications

The fabrication of photonic devices by traditional manufacturing methods has a series of drawbacks, such as cost-intensive, low customizability, low reproducibility, bidimensional construction, lack integration and geometrical constraints [5], [52]. These factors are considered the major challenges to overcome concerning the fabrication of integrated photonic circuits [53], [54], as well three-dimensional lenses and waveguides at microscale/nanoscale [55], [56]. AM is considered a promising manufacturing technique for photonics[5], [57] because it theoretically addresses all the issues associated to traditional manufacturing methods. Similar to other fields, AM has experienced rapid growth in the fabrication of optical devices in the last 20 years.

To date, the most relevant AM technology families employed in optics manufacturing are the MEX, MJT and VPP [52], [58]. Fused deposition modelling (FDM) and Direct Ink Writing (DIW) are the most important concerning the MEX family. As previous mentioned, these techniques are inexpensive and can fabricate large volumes, however high surface roughness and low printing resolution are critical issues hindering their use in microscale optics, and so far, have been only used in the fabrication of THz optics [59]–[61], preforms for optical fibers [7], [62]–[64], and illumination and imaging applications at macroscopic dimensions[65]. Inkjet printing is the most relevant in the MJT

technologies, being adopted in the fabrication of lenses and micro-lenses array. Despite its good optical quality and precision, the technique is limited in printing volume and materials availability, since the development of new materials for Inkjet is challenging, having strict rheological requirements to achieve appropriate resolution. Lastly, VPP-MPP, VPP-UV and VPP-UVM are most important technologies from the VPP family, showing high resolution, and good surface quality. The field has expanded unevenly across VPP technologies, with VPP-MPP being considered matured, while VPP-UV and VPP-UVM are still on their infancy [58]. The main drawback of VPP-MPP has been the printing volume and speed, which has driven research to explore VPP-UV and VPP-UVM as alternatives for printing macroscopic volumes of material, with little compromise to surface quality.

AM has found successful commercial application in the manufacturing of lenses and lenses arrays by companies such as Luxexcel®, Nanoscribe®, and Multiphoton Optics®. Luxexcel® uses a patented MJT platform based on Drop-on-Demand (DoD) technologies to fabricate lenses for smart glasses [66]–[69]. The main advantage of using AM in their case is the easy integration of the lenses with electronics, projection screens, waveguides and LCD displays. Nanoscribe®, and Multiphoton Optics® have developed MPP platforms for microfabrication, with applications in micro-optics, microfluidics, micromechanical systems and integrated photonics, with on-fiber and on-chip printing. Academic research is very rich in terms of applications of AM in photonics[70], [71]. Overall, AM has been employed in the fabrication of waveguides [72] and fiber structures, lenses and lens arrays [73]–[75], grating and diffraction structures [76], photonic crystals, phase modulation elements, SERS (surface enhanced Raman scattering) sensors, metasurface fabrication, solar cells, LEDs [77], optical couplers [78], and many other applications. Particularly, the additive manufacturing of optical fibers and preforms has been a topic of promising research in the last 10 years. As a few milestones, Pereira et al [79] directly printed optical fibers in 2014, Canning et al.[63] drew an optical fiber from a 3D printed preform in 2016, a step index 3D printed preforms has been reported in 2016[7] and non-circular core preforms in 2017 [62]. Furthermore, optical fiber with Bragg gratings[80], photonic crystals[61], [81], [82] and negative curvature cores[59] have been demonstrated.

Despite the promising results reported in the literature, keys problems have been identified in the last years. First, the fabrication of optical devices must have low tolerance concerning shape accuracy and surface roughness. Second, the range of materials available for AM is quite limited. Third, most techniques are currently incompatible with multi-material fabrication. Lastly, the fabrication of individual optical components has been widely reported, however its integration in optical devices must

be further explored [52], [58]. As prior mentioned, MPP technologies are the most advanced in terms of optical devices fabrication, since it can easily reach the surface roughness and shape accuracy requirements, allowing fabrication in arbitrary surfaces. However, this method can only manufacture small volumes, and using only one type of material. Conversely, larger scale manufacturing methods suffer from lower surface quality and shape tolerance. Addressing these issues would allow the one-step fabrication of dense multi-component optical devices, with arbitrary refractive and light guiding geometries combining imaging, detection, actuation and signaling in one single device [58].

f. New materials for AM of photonics

There are many challenges to allow widespread application of AM in the fabrication of photonic devices, and the lack of a variety of materials is one of the main issues. All the above-mentioned examples in the literature concerning AM in photonics are based on mature 3DP materials (polymers, metals and polycrystalline ceramics) [24]. New strategies to print photonic materials in the last 15 years have been studied with emphasis in glasses and most recently in organic-inorganics hybrid (OIH) materials.

Despite the intense use of glass in optical applications, this was one of the last materials to be explored in AM due to the lack of a convenient and inexpensive printing approach or technology [83]. The additive manufacturing of inorganic glasses can be divided in a direct approach, when the raw material is the glass itself, or an indirect, when composite material or glass precursor is printed, and then heat treated to yield final the glass [84]. Historically, the first attempts for AM of glasses were direct approaches, such as fused deposition modelling (FDM) using glass rods [85]–[87], and selective laser melting of glass powder [88] or glass filament [89], however these approaches did not achieve good optical quality and had low resolution. The first indirect approaches relied on the lithography of composites polymer/glass powder [90], [91], however the residual porosity hindered the materials transparency. The first successful approaches that could couple resolution and surface quality comprehended the use of a MPP process with a photocurable SiO_2 nanoparticles composite. In 2018, improvements were made by Nguyen et al. [92] using a DIW (direct ink writing) process with a silica-titania sol-gel. In both cases, post processing through thermal treatment yielded a transparent glass with resolution of hundreds of microns. The most recent strategy for AM of glasses was reported in 2018 by Cooperstein et al [17] using a photopolymerizable resin obtained from a hybrid sol-gel route employing alkoxysilane precursors, yielding a transparent OIH material which could be further heat

treated yielding a glass. To date, this approach have been the only one able to reach high printing accuracy and excellent surface quality [93], and is the foundation for all other publications in the area. Further application of these works in photonics encompasses the additive manufacturing of a silica preform [64].

The primary disadvantage of AM of glasses is thermal treatment at high temperature required, which is not compatible with electronics in order to achieve integrated electro-optical devices. As an alternative, organic-inorganic hybrid materials can be processed at low temperature, and have their optical properties tuned to meet the requirements of active and passive optical devices operating from UV (ultraviolet) to NIR (near-infrared) spectrum [5], [8], [9], making them excellent candidates for integrated active and passive photonic structures [5], [8], [10]–[12]. OIH materials have found numerous applications in photonics such as waveguiding, sensing, lenses, photonic crystals, LEDs and white light sources, random lasers, solar concentrators, luminescent thermometry, photochromic windows, photovoltaics, non-linear optics, plasmonic, electro-optical devices and many others [8], [94]. Despite the wide interest of OIH materials in photonics, the literature available on their AM for photonics is limited to the fabrication of lenses [95]–[114], waveguides [115] and photonic crystals [116]–[120] using alkoxysilane derived materials, with special emphasis on the commercial resin SZ2080 (zirconia-silica sol-gel). Other examples include the use of perovskite/PCL composites for additive manufacturing of LEDs [121], and polymer/ VO_2 composites for solar cells [122].

There are different approaches for synthesizing OIH materials, however the hybrid sol-gel route is the most promising one concerning OIH materials for additive manufacturing of photonics. The main advantage of the sol-gel approach is the mixing at molecular level of organic and inorganic groups at room temperature, hindering phase segregation and being inherently compatible with photopolymerization [123]. However, the design of a transparent OIH requires deep understanding of the chemical reactions during synthesis conditions, since improper control can results in opaque or translucent OIHs [124], [125]. Most works have been limited to silane chemistry since its chemistry and synthesis conditions are easy to control and is well established in literature[123]. Successful examples of OIH materials with good optical quality for photonic application using VPP-UV have been reported for at least 20 years as waveguides and lenses on ORMOCERs/ORMOSILs (i.e. silane hybrid sol-gel) [118], [126]–[129], but no other compositions have been demonstrated.

Vat-photopolymerization (VPP)

a. Fundamentals

The VPP was patented by Charles Hull in the late 1980s and is considered to be the first AM technology. As briefly described, VPP is based on the selective exposure of a light-curing resin to UV or visible light radiation, resulting in localized photopolymerization. To date, VPP is represented by three main techniques, named stereolithography (SLA), digital light processing (DLP), and multiphoton polymerization (MPP), known as VPP-UV, VPP-UVM, and VPP-MPP according to ISO/ASTM 52900:2021 [39]. These techniques differentiate according to the light source employed, and the method to achieve selective exposure. VPP-UV, VPP-UVM, and VPP-MPP use a UV/VIS frequency multiplied laser, a UV/VIS lamp, and an infrared femtosecond laser, respectively, as light sources. The layer construction is accomplished by laser scanning in VPP-UV and VPP-MPP by either moving the object being printed or the laser spot by aid of galvanometer mirrors. VPP-UVM uses a digital micromirror device (DMD) or a liquid crystal display (LCD) to create a mask for each transversal section of the object, printing an entire layer in a single process [24], [25]. The typical setups for VPP-UV and VPP-MPP are illustrated in **Figure 11** (a). The main difference between the two setups is the polymerization volume, since the polymerization in VPP-UV occurs through a linear absorption and all the exposed volume undergoes polymerization. In opposition, the VPP-MPP is based on the multiphoton absorption, which is a non-linear process, with low efficiency, meaning that the polymerization is confined to the focal spot of the irradiation. These differences are illustrated in **Figure 11** (b). Lastly, a setup for VPP-UVM is illustrated in **Figure 11** (c).

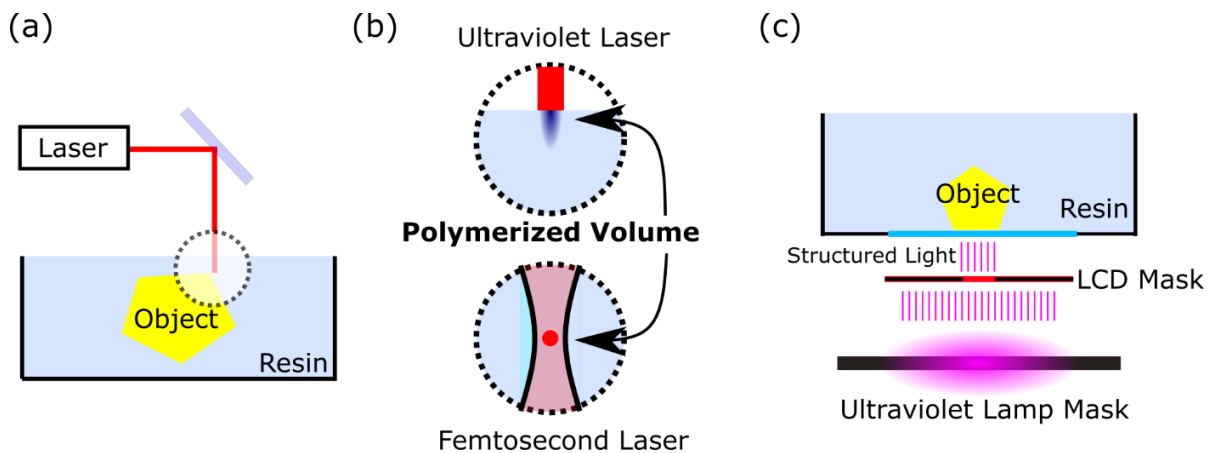


Figure 11. Typical setup for (a) VPP-UV and VPP-MPP, and the difference between their polymerization volumes in (c). A typical VPP-UVM setup is presented in (c).

In the VPP-UV and VPP-UVM process, the object is printed on top of a moving platform, called the build platform. The direction of the platform's movement defines if the equipment has a bottom-up or top-down approach, if the platform moves upwards or downwards during printing [24], as shown in **Figure 12** (a). These differences determine the layer construction direction, and the position of the optical elements in the equipment, which will introduce limitations in terms of build volume (maximum size of printable objects) and might require different printing strategies.

In the top-down configuration, the light source is positioned above the platform. The build platform stays submerged in the vat with a layer of resin between the build platform and the air. Once that layer is printed, the build platform submerges another one layer, allowing the next layer to be printed on top of the previous one. The layer of resin thickness is a user-defined parameter, and it correlates to the Z direction resolution. A delay time is introduced between each layer to homogenize the resins surface, which can be assisted by some type of recoating system, such as a blade or a vat stirrer. Surface homogenization is a key aspect since regions close to the exposed areas suffer from partial photopolymerization, causing variation of density and viscosity (evidenced by a tacky aspect). Thus, heterogeneities are carried to the next layer [130], which can lead to delamination (layer adhesion failures), voids, dimensional distortion, and poor surface quality [24]. Such defects are more prone to occur when printing hollow structures [131]. The need of recoating and surface homogenizing increases the printing time since the process must be slow, causing minimal disturbance on the resin's surface [132]. These steps (print-submerge-homogenize) repeats until the entire object is printed and sank in resin.

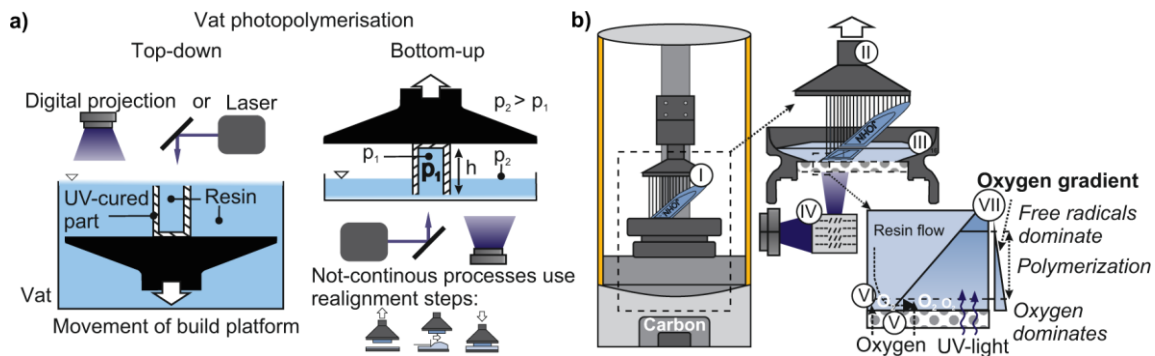


Figure 12. Bottom-up and top-down VPP setups in (a), and continuous liquid interface production (CLIP) setup in (b). [133]

Conversely, the optical setup is located below the vat in the bottom-up configuration, which requires the bottom of the vat to be transparent to the irradiation wavelength. In this setup, the polymerization takes place in the resin confined between the build platform and the bottom of the vat. Similar to the top-down setup, the space between the platform and the vat is a user-defined parameter which defines the Z resolution. Once the exposure occurs, the platform moves upwards, and a new layer is printed, with no need for the homogenization process. When the printing concludes, the object is entirely out of the resin tank. Most commercial equipment (both VPP-UV and DLP) employ the bottom-up approach because of its simplicity. Currently, there is a new generation of bottom-up VPP systems named continuous liquid interface production (CLIP), where the bottom of the vat is permeable to O_2 , creating a dead zone where no polymerization occurs, as shown in **Figure 12** (b). In this process, the platform is constantly drawn instead of printing layer-by-layer, allowing faster printing and smoother details. The bottom-up approach is very convenient for small objects, however printing larger parts can be challenging due to gravity and surface tension, which can cause detachment from the platform, leading to failure [24], [25]. Special strategies are also required for printing high surface area objects, such as tilting the object to reduce the surface area of each layer [25]. In these cases, a top-down approach is preferred, however the vat size limits the build volume and the homogenization process significantly increases the printing time [24].

Printing parts using DLP and VPP-UV require the use of supporting structures. These structures anchor the object to the platform and provide mechanical support for overhanging features. Furthermore, supporting structures reduce the warping caused by direct adhesion of the printed part to the platform. Most commercial platforms have an in-built function to add these supporting structures to the digital drawing, however the planning and positioning of support structures is also part of the design process, because they must be removed during post-processing. A build platform is not required in the case of VPP-MPP, because the part is printed directly inside the resin, however, it requires a support structure for fixing the part during the process [24].

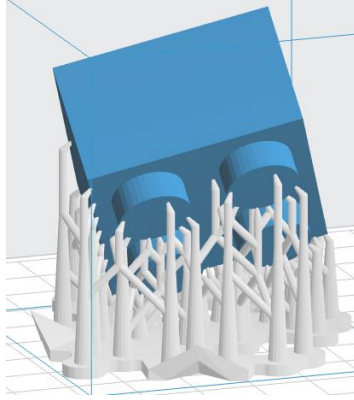


Figure 13. Drawing of support structures overlaid with the digital design of the object to be printed [133]

The absence of a scanning pattern was one of the main issues in the early days of the VPP technique [24]. The photopolymerization process is associated to shrinkage, creating localized stresses that can result in warping and cracking. The laser scan pattern is a fundamental aspect of VPP-UV and VPP-MPP, because it controls the distribution of these stresses and adhesion between layers. In the beginning, a trial-and-error approach was employed until acceptable results were achieved, which resulted in low success rate. The first scan pattern introduced into the market was the WEAVE, in 1990, where a mesh is created by fabricating one layer by scanning lines parallel to one axis, and the following layer by scanning lines in the perpendicular axis. The scan direction was kept constant between two layers, and it drastically improved the printing quality and success rate. Despite the improvements, deformation problems were still frequent, which originated the STAR-WEAVE pattern in 1991 [24], solving virtually all problems of the previous technique, by alternating the scanning direction from one layer to another and intertwining the layers, as illustrated in **Figure 14**. With the advent of epoxy-based resins, the ACES pattern was introduced to achieve better accuracy and higher polymerization given the slower kinetics associated to these new resins. The ACES pattern is actually a collection of different scan patterns, that give more control of the printing process to the user [24].

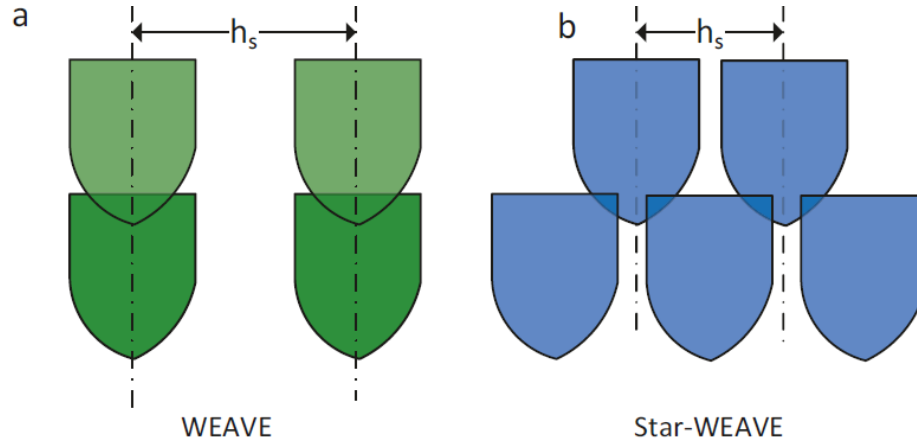


Figure 14. Positioning of each line scan for two layers using a WEAVE and Star-WEAVE laser scan pattern. [24]

b. The laser-resin interaction

Modeling the laser-resin interaction enables the selection of optimal exposure conditions to achieve the desired part/object, because the platform vertical movement must match the layer thickness. The Jacob's work curve is a widely adopted mathematical model describing the relationship between energy dose (E_{max}) and the thickness of the cured layer, named cure depth (C_d), as shown in Equation 1 [24], [134], [135]. The model was derived in the early 60s by describing the light penetration using the Beer-Lambert law with a characteristic penetration depth (D_p) value, and a laser with gaussian profile scanning at constant speed. The model assumes the existence of a critical energy value (E_c) where the resin reaches a gel point [134], [135], and behaves like a solid.

$$C_d = D_p \ln \frac{E_{max}}{E_c} \quad (1)$$

E_{max} is the peak exposure and is calculated from Equation 2.

$$E_{max} = \sqrt{\frac{2}{\pi}} \frac{P_l}{W_o V_s} \quad (2)$$

where P_l is the laser power, V_s is the laser scanning speed and W_o is the beam diameter.

Experimentally, one measures E_{max} (laser intensity) and C_d , and fits the data to extract the D_p and E_c parameters, which are intrinsic to the resin, wavelength, and exposure conditions studied [24]. These parameters allow the resin to be printed in any other VPP equipment operating with the same laser wavelength, power and exposure conditions employed. Most VPP-UV system manufacturers,

however, lock the exposure setting on their equipment so the printer can only fabricate with the manufacturer's resin. In addition, the Jacobs work curve parameters for most commercial resins are hardly available. Reference parameters for commercial resins were studied by Bennett in 2016 [136], showing a remarkable variation on E_c and D_p parameters from product to product, as shown in **Table 1**.

Table 1. Typical E_c and D_p values for commercial VPP resins measured at 365 and 405 nm. [136].

Resin	D_p (μm)		E_c (mJ/cm^2)	
	365 nm	405 nm	365 nm	405 nm
PR48®	42	53	18.3	6.3
VeroWhitePlus®	43	145	0.7	1.9
Formlabs Clear®	146	192	5.2	1.,6
TangoBlackPlus®	95	151	2.4	4.1
VeroClear®	186	568	2.1	6.9

The Jacob's work curve model oversimplifies the photopolymerization reaction because its only assumption concerning the photochemical process is the existence of a critical energy parameter. This assumption implies that the photopolymerization is a time independent process, and that the gel point is a well-defined parameter. This is not true because the polymerization is a highly dynamic process with numerous parallel reactions [137], [138], and affected by many factors such as the dependence of kinetic constants on light intensity [139], presence of scattering centers [140]–[144], diffusion of active centers and monomers [145], [146], photobleaching of photoinitiator fragments [147], oxygen inhibition [146], [148], heat diffusion [149], self-focusing effects [150], polymerization shrinkage and cyclization reaction [151]–[153], and the gel effect [137], [138], [154], [155]. Consequently, the work curve model yields penetration depth and critical energy values which are valid only for the applied exposure conditions. Nonetheless, the model is widely adopted due to its simplicity.

The lack of chemical fundamentals on the equation was addressed by Lee et al.[156], who derived a work curve based on steady-state models to describe the photopolymerization kinetics, obtaining Equation 3 and 4:

$$E_c = \frac{\alpha\beta}{\sqrt{[PI]}} \quad (4)$$

$$Dp \propto \frac{1}{\epsilon[PI]} \quad (5)$$

Where α and β are a combination of photochemical and processing parameters, respectively, and ϵ is the molar absorptivity. However, their model disregards polymerization inhibition effects before reaching steady state conditions and does not address how laser power affects the work curve, since the polymerization rate is dependent on the light intensity by a power law [157]. Further addressing such problem, Uzcategui et al [139] proposed a modification on the work curve in the form of Equation 6

$$C_d = \frac{Dp}{n} \ln \frac{t \cdot I^n}{Ec} \quad (6)$$

where n is an exponential factor between 0 and 1. Thus, the authors proposed that both polymerization rate dependence on light intensity and the induction period can be expressed by a single exponential factor adjusting the intensity parameter, however we highlight that Wydra et al.[158] have demonstrated that the main hypothesis supporting their modified model is not accurate because of the bimolecular termination mechanism. Nonetheless, their model can still provide good fitting to experimental data.

c. Photopolymerization

Photopolymerization refers to a photoactivated polymerization process initiated by a photoinitiator, which are molecules that, when exposed to a proper range of wavelength, undergo an electronic transition, yielding an unstable excited singlet or triplet states [159]. The excited molecule undergoes scission, generating species that can start the polymerization process. Available photoinitiators can generate cationic species, which can initiate the polymerization of epoxy and vinyl-ether functional groups, or radical species, which can initiate the polymerization of methacrylate and thiol-ene groups [160].

The free-radical photopolymerization mechanism for acrylate-based monomers is presented in **Figure 15**. When irradiated, the photoinitiator undergoes photo-scission generating radical species, which are highly electrophilic and are promptly attacked by the electronic density of the C=C bond present in the acrylate. The electrophilic attack breaks the double bond and forms a new bond between the radical species and one of the carbons from the C=C bond [160]. The second carbon atom (which did not form new bonds upon scission) becomes a radical species susceptible to electrophilic attack

from a different acrylate group [159]. This new radical is defined as the propagating or active center. This chain of reaction from the irradiation to the formation of the active center is defined as the initiation step in the photopolymerization, which is then followed by either propagation, or termination steps. Propagation refers to the chain reaction of the active center with another monomer, adding a new monomer to the growing molecule and transferring the active center to the newly added monomer. This reaction repeats multiple times, resulting in a polymeric chain [161].

The free-radical polymerization process ends with the termination step, by deactivating the active center. There are multiple reaction pathways, but the most important ones are recombination, disproportionation, primary recombination, and oxygen inhibition [161], [161], [162]. The first three comprehend the reaction of two active centers, while the latter consists in the reaction of one active center with a radical-scavenging molecule (O_2). In recombination, the two active centers form a covalent bond between the two growing polymeric chains, annihilating the radical centers. In disproportionation, one of the active centers abstracts a hydrogen from the second active center, annihilating the first active center. Then, the second active center forms a double bond with carbon that had its hydrogen abstract, resulting in a polymeric chain with a unsaturation. Primary recombination is similar to the recombination mechanism, however one of the active centers is a free-radical generated from the photoinitiator instead.

Oxygen inhibition comprehends the reaction of a radical species (active center or primary radical), with molecular oxygen, resulting in active center that has very low reactivity [163]. Oxygen inhibition is a highly efficient reaction, which creates an induction time where no polymerization occurs, until molecular oxygen is depleted, which is typically represented by a decrease in concentration of three-orders of magnitude (from $\sim 10^{-3}$ to $\sim 10^{-6}$ mol.L $^{-1}$ [164]). Oxygen inhibition plays a major role in VPP top-down approach since the resin's surface is saturated with O_2 , leading to incomplete and inefficient polymerization, which can cause printing defects. To overcome such problem, an excess of photoinitiator is employed, so that all molecular oxygen is quickly depleted.

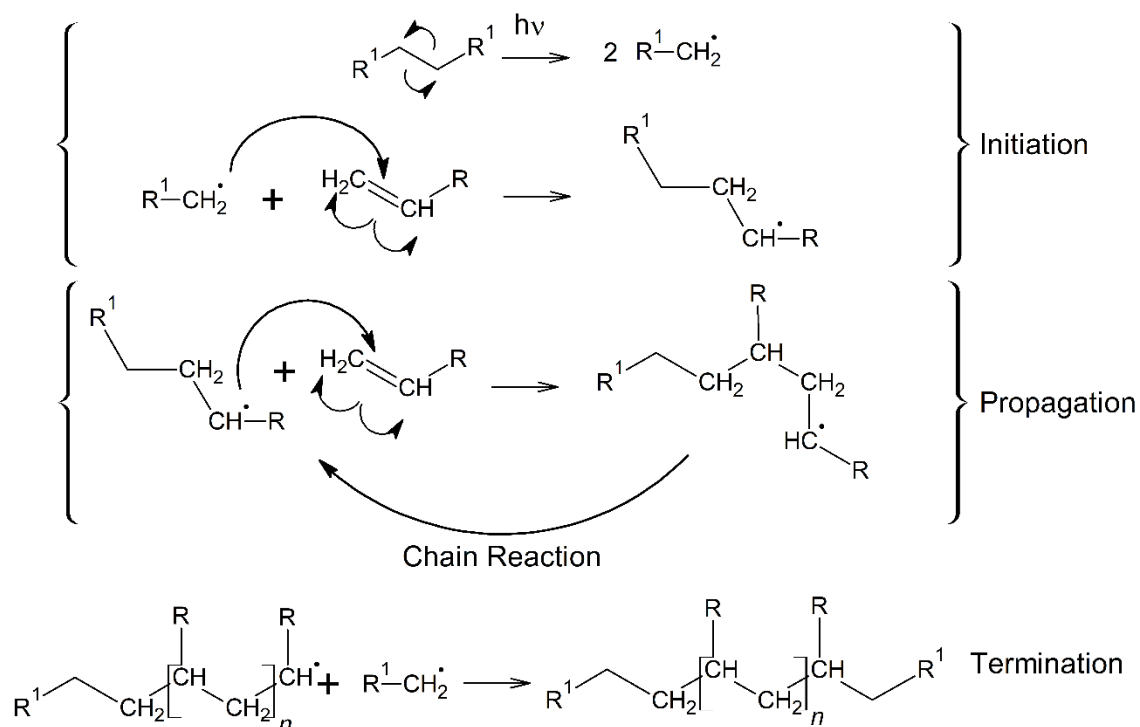


Figure 15. Typical radical polymerization reaction steps.

The cationic photopolymerization of epoxy and vinyl ether monomers is presented in **Figure 16**. Cationic photoinitiators are typically iodonium salts that undergo photo scission, releasing a non-nucleophilic anion [160]. There are many proposed reaction pathways following the formation of the anionic specie [159], [163], however the most common path is the hydrogen abstraction from monomer or solvent molecules, forming a super-Bronsted acid [165], that is a proton donating species. The proton is transferred to the heteroatom in the epoxy ring/vinyl-ether, linearizing the epoxy ring or promoting the scission of the double bond in the vinyl-ether, resulting in a carbocation species [159], which becomes the active center. The reactions from irradiation to the formation of the carbocation comprehends the initiation step. Similar to free-radical photopolymerization, initiation is followed by either propagation or termination steps. In propagation, the carbocation reacts with the heteroatom of other monomers, forming a covalent bond and transferring the active center to a new monomer [160]. The chemical pathways for termination are different compared to free-radical photopolymerization because it typically occurs by rearrangement with the counter anion. Other processes such as hydrogen abstraction, disproportionation, recombination or chain transfer reactions [160] do not effectively terminate the reaction, but only stop the growth of that polymeric chain, while generating a

new active center. A fundamental difference between cationic and radical polymerization is that inhibition of cationic polymerization occurs by nucleophilic attack of species such as water [159].

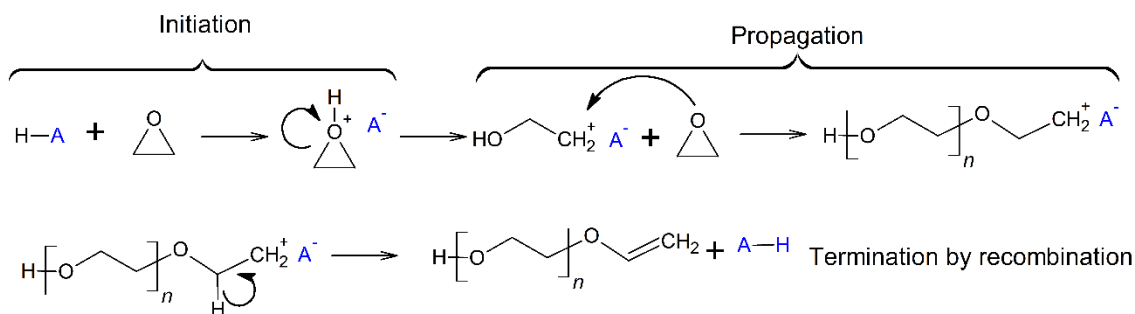


Figure 16. Typical photopolymerization mechanism for epoxy polymers.

The polymerization of resins for VPP is a very complex phenomenon, because the Trommsdorff–Norris effect, also known as gel effect [137]. The gel effect refers to the autoacceleration and autodeceleration of the polymerization reaction due to the formation of a three-dimensional polymeric network and entanglement of polymeric chains, restricting molecular mobility. Polymeric chains in solution tend to coil, forming primary gel particles, favoring intra-particle over inter-particle polymerization as the active centers are much closer to unreacted monomer species in the same chain [137], [155]. In this case, the propagation reaction is favored while the termination reaction is hindered, since the latter involves the reaction of two polymeric chains (which have far less mobility) while the first involves one polymeric chain and one monomer, which can easily diffuse through the medium. This leads to the autoacceleration behavior, that is, a remarkable increase in the polymerization rate. The second phase of the gel effect takes place when the network percolates through inter-particle polymerization, hindering segmental mobility and monomer diffusion, slowing down the propagation reaction. This is the autodeceleration behavior, and results in incomplete polymerization [137], [138], [166].

Resins for VPP require a large concentration of multifunctional monomers, meaning that the formation of a three-dimensional network occurs at very early stages of polymerization. As a consequence, the gel effect manifests at very early stages during the polymerization process, and the polymerization kinetics change dramatically as the reaction progresses. Furthermore, the gel effect is based on the micro heterogenous nature of the polymerization reaction, which results in a polymeric micro-heterogenous structure as well. Thus, modelling the photopolymerization process is quite challenging, despite the simplicity of the polymerization reaction.

d. Resins for VPP

A resin for VPP is composed by multifunctional monomers and oligomers (monomers with molecular weight in the range of 1000 g/mol), photoinitiators, and additives. The development of resins for VPP is simple, requiring that the resin undergoes photopolymerization and is chemically stable during the printing process, which can take hours. Commercial resins are a combination of acrylate- and epoxy-based monomers with their respective photoinitiator system [24]. Acrylates have higher polymerization rates, higher linear retraction (20% while epoxies shows retraction of 10%), and no dark cure (photopolymerization once exposition is interrupted) compared to epoxy and vinyl ethers [48], [49]. The use of acrylate and epoxy based monomers has synergistic effects during the additive manufacturing process [24]. First, the polymerization of acrylates is very fast, allowing shape consolidation with minimal mechanical strength, which are further developed by the dark cure of epoxy monomers, giving the final mechanical properties [24]. The slower polymerization of epoxy allows low viscosity to be maintained for longer periods during the free-radical polymerization of acrylates, improving double bond conversion [167]. Also, the heat from acrylate polymerization accelerates epoxy polymerization, and inhibition effects due to water and oxygen are reduced [167]–[169]. These mixed systems also reduce the polymerization shrinkage, reducing residual stress and improving the mechanical properties. Residual stress is responsible for fractures, delamination, warping and other printing problems, and can result in birefringence[170], [171].

Monomers for VPP resins are multifunctional [48] [172]–[175], meaning that they possess more than one polymerizable group in the same molecule. They are a core aspect of a resin's formula since the polymers final structure plays a major role in the desired properties. The presence of multifunctional monomers forms a thermoset or highly crosslinked polymer [135] that is insoluble in the monomer. Furthermore, acrylates and epoxy undergo different polymerization mechanisms, forming two (or more) intertwined crosslinked polymeric networks [176]. This molecular structure avoids polymeric phase segregation, enhancing the mechanical properties and hindering swelling [177]. The final molecular structure is a special kind of polymeric blend namely interpenetrating polymeric networks (IPN)[176], [177] as shown in **Figure 17**.

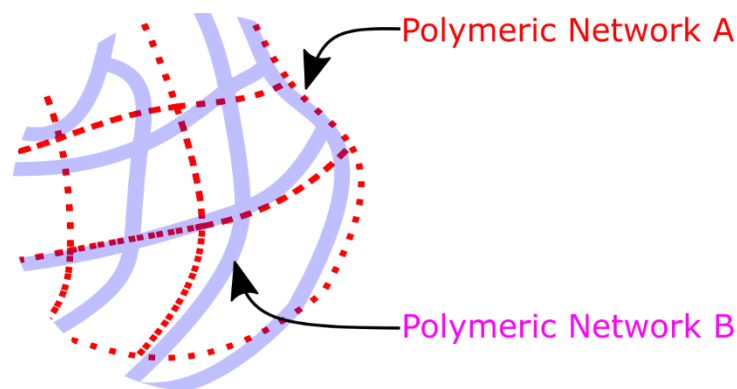


Figure 17. Representation of the structure of an interpenetrating polymeric network (IPN).

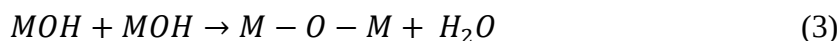
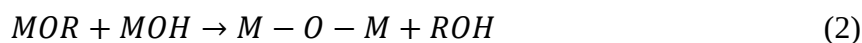
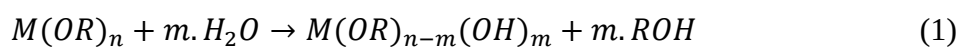
In addition to monomers, additive are used to control the absorption properties of the resins and viscosity. Opacifiers (UV absorbers) are commonly used to adjust the penetration depth of resin to match specific requirements by the manufactures, while solvent can be used to adjust the resins viscosity [24]. Typically, the viscosity of a commercial resin is between 200 and 8000 cP [135], however the rheological properties are not crucial, although high viscosity can slow the photopolymerization process. Lastly, appropriate photoinitiators are introduced in concentrations up to 10% w.t. [178], [179] to minimize oxygen inhibition [164]. The selection of photoinitiators is based on the irradiation wavelength and type of monomer employed. Because acrylates and epoxy monomers are used, at least two type of photoinitiators are present, which generate a photosensitizing effect, where the generated free-radical species can activate the cationic photoinitiator, providing comparable conversion rates between the epoxy and acrylate polymerization [180]. Although there is a diversity of formulations, one of the biggest problems related to 3D printing by VPP is stablishing the relationship between materials properties and the resin composition [48].

Sol-gel route

a. Fundaments on sol-gel

The sol-gel route is a soft-chemistry synthesis approach that started being explored in 1930s [181]. The chemistry of sol-gel is based on the reactions of hydrolysis, oxolation and ololation (the latter two representing the condensation reactions) of chemical precursors, mostly metal alkoxides, as showed in reactions (1), (2) e (3), respectively [182]. The condensation reaction progressively forms M-O-M bonds (where M represent the metallic atom of the alkoxide source) resulting in a tree-dimensional network and in a colloidal suspension named sol, that further percolates to result in a gel

with a liquid phase trapped in the structure [182]. Post processing can include drying and calcination, allowing the elimination of organics and solvents. The microstructure can be controlled to yield xerogels, aerogels, or even dense monolithic parts depending on the drying process to meet the needs of a given application. The sol-gel route can synthesize inorganic materials under mild conditions of processing, such as low temperature (<200°C) and open atmosphere, which makes it compatible with organic chemistry [13]. Currently, the sol-gel route is employed in various applications such as drug distribution systems [183], [184], imaging and tissue engineering [184]–[190], development of fuel cells [191], ceramic lithography [192], synthesis and coating of nanoparticles [193], [194], 3D printing [195], functional coatings [196], [197] and a diversity of other applications [198].



b. Controlling the kinetics of condensation

The main challenge of the sol-gel route is controlling the hydrolysis and condensation reaction. Ultimately, the main goal of controlling the hydrolysis and condensation kinetics is to achieve the higher hydrolysis and condensation degree before gel formation occurs. The sol-gel route is typically described using a bimolecular nucleophilic substitution mechanism (S_n2) [182], although there is evidence for the participation of unimolecular nucleophilic substitution (S_n1), and addition-elimination mechanisms [199]. Based on these mechanism, the key factors determining the kinetics of hydrolysis and condensation are the reactants choice (type of alkoxide), temperature, solvent, presence of complexing agents and the pH [182], [200].

The reactivity of each metal alkoxide will depend on the coordination number (CN) of the metal atom in the alkoxide, the electropositivity of the metallic atom, the size of the alkoxide groups, and the maximum CN that the metal atom can achieve [13], [15], [16]. For instance, the higher the electropositivity, the more susceptible the alkoxide is towards nucleophilic attack, meaning that hydrolysis and condensation are highly favored. The size of the alkoxide group is another important factor because it creates steric hindrance for hydrolysis and condensation, meaning that the reaction becomes slower as the alkoxide groups increase in size. Lastly, the greater the difference between the

CN of the metal in its alkoxide form and its maximum values, the higher the reactivity. The latter occurs because the metallic atom undergoes an expansion of its coordination sphere during the hydrolysis and condensation reactions, resulting in more sites available for reaction. The effect of CN is far more prevalent in transition metals alkoxides, such as zirconium, titanium, aluminum, and others. For these alkoxides, the addition of complexing agents to the reaction media can slow down the reaction, because they coordinate to the metallic atom, partly expand the coordination sphere, and create steric hindrance.

The solvent also plays an important role, because it can compete with the hydrolysis and condensation reactions. For instance, most sol-gel synthesis is performed using a combination of alcohol and water since the alcohol can compete with water during the hydrolysis, and with other alkoxide species during condensation, slowing down the reaction rate [182]. The pH is a very important factor that has a twofold effect. First, high pH and low pH increases the hydrolysis and condensation rates by promoting more nucleophilic species and more stable leaving groups during the substitution reaction, respectively. Second, the pH affects the charge balance on the surface of colloidal particles which have an isoelectric point around pH 5 for silica-based sol-gel. Thus, in acidic environments, the sol tends to be more stable compared to basic medium, since these colloidal particles are less favored to condense [182].

c. The hybrid sol-gel route

The hybrid sol-gel route is a special case of sol-gel chemistry employed in the synthesis of organic-inorganic hybrid (OIH) materials. It has received wide attention in the last 5 years because it is inherently compatible with VPP technologies, and has been the main approach to 3D print glasses with high resolution [84]. The hybrid sol-gel route employs chemical precursors with a non-labile functional organic group that can react through polymerization, such as acrylate and epoxy. Because of its mild conditions of processing, this chemical precursors can condense to form a tridimensional inorganic network, and polymerize to form a parallel polymeric network, resulting in OIH materials [13]. Typical examples of alkoxysilanes employed in this route are presented in **Figure 18**. This class of materials were widely explored in the synthesis of silicate-based OIH materials under the name of ORMOSILs (organically modified silane) and ORMOCERs (organic modified ceramics) [201]. By engineering the structure of these materials, their mechanical, optical and other physical-chemical properties can be tuned for different applications such as contact lenses, gas barriers and anti-scratch coatings[202],

synthesis of nano coated particles[203], production of functional coatings[204]–[207], photo catalysis[208], [209], protective coating for space instruments[210], light sensors [211], and the lithography of oxide ceramics[212]–[216]. Furthermore, the development of hybrid materials from the sol-gel route is of particular interest for the development of biomimetic, nano-structured, or multifunctional materials[181], [217]–[220]. More recently, the hybrid sol-gel method has been applied in additive manufacturing of ceramics, glasses and OIH material [221].

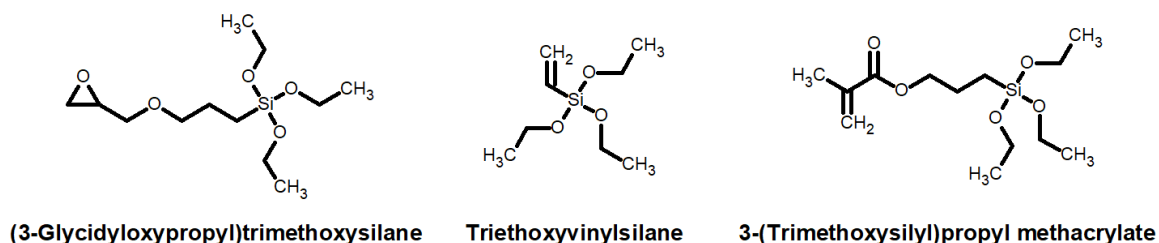


Figure 18. Examples of functional alkoxy silanes commonly used in the hybrid sol-gel route.

The selection of appropriate chemical precursors is of uttermost importance in the hybrid sol-gel route. The functional organic group must be stable against hydrolysis, that is, the chemical bond between the organic group and the moieties involved in the sol-gel chemistry must be strong, so that the organic groups responsible for the formation of the polymeric network are not eliminated during condensation [13]. In the case of silicon, tin, phosphor, lead or mercury alkoxides, the M-C bond is more stable against hydrolysis than M-O-C[222] due to the electronegative character of the central atom and the saturated coordinating sphere, making it less susceptible to the nucleophilic attack by water. Thus, in the case of these alkoxides, the polymerizable functional groups must have chemical bonds of type M-C.

Transition metals alkoxides such as zirconium, titanium, aluminum, cerium, among others, are far more challenging in the hybrid sol-gel route because both the M-C and M-O-C bond are very susceptible to hydrolysis due to the low electronegativity and CN [223]. One of the main strategies to use transition metal alkoxides in hybrid sol-gel route is to use complexing agents such as β -diketones, which show keto-enol tautomerism, as shown in **Figure 19** [184], [222]–[225], and bind to the metal (**Figure 20**), expanding their coordinating sphere and causing hysterical impediment against the nucleophilic water attack. These complexing agents are specially selected to have polymerizable groups, such as 2-methacryloxyethylacetoacetate (MAEAA) and acrylic and methacrylic acids [212]–[215], [223], [226]–[230].

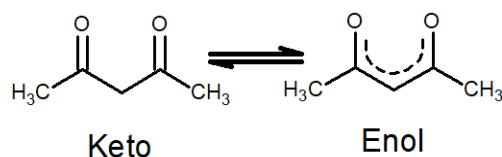


Figure 19. Keto-enol tautomerism of acetylacetone.

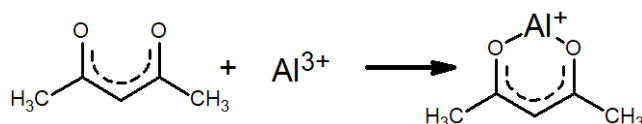


Figure 20. Chelating effect of acetylacetone to aluminum ion.

d. Aluminum-phosphate hybrid sol-gel materials

Aluminum-phosphate (AIP) based materials have high solubility for lanthanide ions, preventing clustering and concentration quenching, making them ideal hosts for luminescence applications, [19], [20]. As a matter of fact, glasses based on AIP, such as silicate-aluminum-phosphate are staple materials for telecommunications as fiber lasers and signal amplifiers [231]. Thus, aluminum-phosphate OIH materials are a class of materials of great interest as matrices for dispersion of lanthanide ions for the fabrication of active optical devices. However, the literature available on AIP OIH materials is quite scarce because their synthesis is challenging. For instance, most reports in the literature are related to metal organic frameworks (MOFs) [232], which are opaque, and there are no reports of transparent AIP OIH materials. In this regard, the hybrid sol-gel route is one of the most promising approaches to achieve transparent AIP OIH materials compatible with VPP. However, obtaining AIP based materials via the sol-gel chemistry is quite challenging because its precursors are either too reactive or unreactive, not to mention the selection of aluminum and phosphate precursors with non-labile polymerizable pendant groups.

Phosphate are poor gel-formers, lacking self-condensation ability (formation of P-O-P) and their alkoxides are very stable towards hydrolysis [21]. Phosphorus high electronegativity hinders nucleophilic substitution (hydrolysis) [21], [233] and self-condensation in acid medium. The small positive charge on phosphorus also restricts homocondensation and hydrolysis in basic medium [21]. Consequently, phosphorus sol-gel chemistry is based on heterocondensation with other metals, often transition metals, since their small electronegativity favors the formation of P-O-M bonds[234], [235]. Phosphorus alkoxides are of limited use in sol-gel and preference is given to phosphoric and

phosphonic acids, phosphorus halides, phosphorus pentoxide or phosphites, which are very reactive in the presence of most metal alkoxides [13], [236], with uncontrolled condensation [234] leading to precipitation instead of gel formation[237]. Acidic phosphate group (P-O-H) are the main responsible for condensation reactions, meanwhile organic groups (P-O-R and P-C) reduces condensation rate, since the bond is unreactive and creates steric hindrance[233]. Conveniently, the stability of P-C and P-O-C bonds[21] allows us to select polymerizable organic groups to be used in the hybrid sol-gel synthesis as well. Thus, appropriate phosphate sources for sol-gel synthesis of AIP OIH materials, should present a good balance of P-O-H and P-O-C/P-C bonds, with the polymerizable organic function attached through either the P-O-C or the P-C bond.

Aluminum precursors for sol-gel, such as alkoxides (Al-O-C) and organometallics (Al-C), are highly unstable due to the unsaturated coordination sphere and high electropositivity of aluminum. In this case, aluminum alkoxides can be chemically modified with chelating agents to improve stability and adjust its reactivity towards condensation [13]. Chelating agents are molecules to bind using different sites to the metal atom, stabilizing it through steric hindrance and the chelating effect (multiple bonds have to broke in order to unbind the chelating agent to the metal) [13]. β -ketoester or carboxylic acids are common chelating agents for metal alkoxides. Furthermore, chelating agents with a polymerizable group, such as acrylic acid (AA), acetylacetone (ACAC) and 2-methacryoxyethylacetoacetate (MAEAA) can be selected to result in hybrid sol-gel materials[236], [238], [239]. To the best of our knowledge, there are not concise and broad studies regarding the stability of modified metal alkoxide for sol-gel synthesis.

CONCLUSION AND OUTLOOKS

In this project, we developed aluminum-phosphate-based hybrid materials using the sol-gel route for additive manufacturing. We characterized in-depth the structure of these materials using solid-state NMR. These materials are candidates for the fabrication of active and passive additive manufactured photonic devices. For this project, we employed a custom-made VPP system operating under intermittent exposure conditions. We developed a mathematical model describing the exposure profile outputted by this custom-made VPP setup, since its operating principle greatly differs from commercial platforms. Then, these new materials were 3D printed after characterizing their VPP parameters and photopolymerization kinetics. Lastly, we examined the optical homogeneity and anisotropy of additive manufactured elements from these materials.

Initially, we explored a series of reactants and synthesis protocols to achieve photopolymerizable aluminum-phosphate sols suitable for VPP. The first series of materials obtained were reported in **Chapter 1**, comprehending organic-inorganic hybrid (OIH) materials composed by poly (2-hydroxyethyl methacrylate) chains with aluminum-phosphate groups covalently bonded to the polymeric backbone, as revealed by solid-state NMR, and infrared spectroscopy. The connectivity between aluminum and phosphate groups was investigated in-depth by solid-state NMR, showing strong dependency to the aluminum to phosphorus ratio. Ultimately, these inorganic units provide numerous crosslinkers, resulting in a highly interconnected and interlocked inorganic/organic structure. The obtained materials are stable solutions that can be photopolymerized to yield OIH materials optically transparent between the 420 nm - 1100 nm range with low volumetric retraction compared to methacrylate polymers, making them ideal candidates for additive manufacturing via VPP. However, these materials suffer from poor transmittance in the near-infrared region (NIR) due to the high organic content of these matrices.

We addressed these issues by developing the materials presented in **Chapter 2**, where we substituted the 2-hydroxyethyl methacrylate by a common alkoxysilane precursor, resulting in aluminum-phosphate-silicate OIH materials. Similarly, we obtained photopolymerizable and stable solutions compatible with VPP technologies, resulting in transparent hybrid materials with high inorganic mass content and improved transmittance in the NIR. We investigated the structural evolution with Si concentration for polymerized samples with different Al:P ratios by means of solid-state NMR,

SEM and phase contrast AFM imaging. An extensive solid-state NMR analysis showed that these materials follow the build-up principle with aluminum-phosphate species and alkoxy silane chains acting as fundamental building blocks. The Al:P ratio dictates the hetero-condensation of aluminum and phosphate precursors, resulting in linear aluminum-phosphate units with monomeric or dimeric nature depending on the Al:P ratio. The dimeric structure favors alkoxy silane homo-condensation, resulting in separate silicate and aluminum-phosphate inorganic networks, while the monomeric structure allows Al-O-Si hetero-condensation, resulting in an inorganic network composed by aluminum-phosphate units interconnected by silicate chains. These structural features present these materials as potential candidates to immobilize lanthanide ions for developing active optical components.

In **Chapter 3**, we tested a mathematical model describing the exposure profile outputted by the custom-built printer employed in this work, allowing us to model the laser-resin interaction in this equipment, and to correlate the printing parameters measured for our materials with those of commercial AM setups. We observed that our proposed model has the same logarithmic dependence of Jacobs work curve (laser-resin interaction model widely employed), with the addition of a factor describing the overlap from adjacent pulses. This study led to two important observations: first, it is possible to correlate the printing parameters measured for our resin in this equipment and recalculate the values to other commercial setups; second, there are limits concerning the applicability of the Jacobs work curve model in the new generation of VPP platforms. Furthermore, we identified that this printing system can, theoretically, print faster compared to commercial platforms under specific conditions of beam diameter and overlap between pulses.

In **Chapter 4**, we explored the additive manufacturing of the aluminum-phosphate-silicate resins studied in **Chapter 2**. We studied the evolution of the 3D printing parameters of these materials (critical energy and penetration depth), and of the photopolymerization kinetics with light intensity and silicate concentration. Furthermore, we used our experimental data to validate a photochemical model published in the literature describing the VPP process. The model predicts that $E_c \propto (k_t^{1/2}/k_p) \ln p_c$ and $D_p \propto \epsilon$, where k_t , k_p , p_c , and ϵ are the kinetic constant of bimolecular termination, kinetic constant of propagation, critical conversion, and absorption coefficient at the laser wavelength, respectively. Our study reveals that both $E_c \propto (k_t^{1/2}/k_p)$ and $D_p \propto \epsilon$ relationships hold true and there is a link between the critical energy and the kinetic constants describing the polymerization process of a given material.

Lastly, in **Chapter 5**, we studied the refractive index distribution and the presence of optical anisotropies in 3D printed lines (the fundamental structure fabricated by VPP) fabricated using one of the aluminum-phosphate-silicate resins studied in **Chapter 2**. Micro-Raman mapping showed a gradient of polymerization degree present in the lines, where smaller C=C conversions were achieved as the light intensity decreased (deeper light penetration and farther from the beam center), however, this gradient did not lead to significant variation of refractive index ($<10^{-4}$). Further studies by polarimetry, revealed the presence of optical anisotropies in these lines; however, these anisotropies did not arise due to molecular alignment, as showed by polarized micro-Raman mapping, indicating that the birefringence arises from the shear stress perpendicular to the scan direction due to the inflow of monomer towards the polymerization spot. To the best of our knowledge, this is the first study on the optical properties of 3D printed parts.

Overall, the results of this Ph.D. project present a myriad of prospects. For instance, we explored the synthesis and characterization of sol-gel hybrid materials with exotic compositions, whose synthesis is known to be challenging. Not surprisingly, we are the first to report these kinds of materials, that is, stable photopolymerizable resins that result in transparent aluminum-phosphate OIH materials. As prior mentioned, these materials could be interesting hosting matrices of lanthanide ions for the development of active optical devices, however further study must be done address its feasibility. Furthermore, these materials still have an organic nature, which has deleterious effects on transmission properties at NIR and could prevent the application of these materials in photonics. There is still room for improving the optical properties of these materials.

Concerning the additive manufacturing, we observed that further effort would be required to better understand the relationship between photochemistry and VPP. The study of the 3D printing parameters of our materials and their kinetics of photopolymerization provided insight into the link between process modelling and the chemical reactions involved. This relationship is a fundamental gap in the additive manufacturing area, which would ultimately lead to more precise models, simulations and understanding of the relationship between properties and processing conditions in VPP. Similarly, our mathematical model describing the exposure profile of our custom-made intermittent exposure VPP setup addressed another major gap in the literature, since the Jacobs work curve is still employed to model the laser-resin interaction, even thou its development assumed the use of continuous laser sources that became totally obsolete in the last 30 years. The model that we developed is very simplistic, and ignores a series of different dynamic effects associated to the

photopolymerization that can deeply affect the additive manufacturing, requiring additional investigations to include these factors.

Finally, we established a protocol to measure optical anisotropies and inhomogeneities in 3D printed materials. So far, all published works concerning additive manufacturing for photonics did not address the anisotropic nature of the additive manufacturing process, and our results demonstrate that further application of VPP techniques for additive manufacturing of photonic materials requires additional effort into elucidating the optical properties at microscale in these materials. Our work provided insight into the nature of these optical heterogeneities and anisotropies. Nonetheless, further understanding of its origins, improvements in the methods for quantification and mitigation strategies must be studied.

RESUMO EXPANDIDO

A MA é uma tecnologia promissora para a área de fotônica, e tem recebido ampla atenção na última década como um método para contornar as limitações geométricas e de integração presentes em métodos tradicionais de fabricação, o que poderia permitir uma nova geração de dispositivos ópticos integrados. As tecnologias MA para fotônica devem ser capazes de fabricar objetos com alta resolução (<10 μm) e elevada qualidade de acabamento de superfície, que são condições atendidas por poucas tecnologias de MA. Neste quesito, a família de técnicas de fotopolimerização em cuba (“*vat photopolymerization*” VPP) é uma das poucas que atendem a tais requisitos e, embora existam inúmeros exemplos na literatura sobre o uso da VPP em fotônica, existem poucas investigações fundamentais sobre a qualidade óptica das peças produzidas, especialmente no que tange a homogeneidade e anisotropia óptica, visto que a MA é um processo fundamentalmente anisotrópico.

A disponibilidade de materiais compatíveis com a VPP é um dos principais problemas limitando ampla aplicação dessa família de técnicas no domínio da fotônica. A VPP constrói objetos por meio da fotopolimerização seletiva de uma resina, formando cada secção transversal do objeto. Entretanto, o mecanismo de fotopolimerização é restrito a polímeros, o que limita a aplicação em óptica de objetos fabricados por VPP as regiões do visível e de terahertz do espectro eletromagnético, uma vez que os grupos orgânicos apresentam elevada absorção na região do infravermelho próximo. Dessa maneira, o desenvolvimento de novos materiais compatíveis com a VPP para aplicação fotônica se transformou em um campo emergente e de grande relevância. Nos últimos anos, tem havido intensa pesquisa para permitir a MA de vidros inorgânicos via VPP, que é um material clássico no desenvolvimento de dispositivos ópticos ativos e passivos. A principal desvantagem, no entanto, é que todas as abordagens disponíveis requerem tratamento térmico a alta temperatura, dificultando a construção de dispositivos eletro-ópticos integrados. Nesse contexto, o uso de materiais híbridos orgânico-inorgânicos (HOI) com VPP surgiu como uma alternativa aos materiais poliméricos e vidros inorgânicos, uma vez que suas propriedades ópticas podem ser ajustadas para atender aos requisitos de transmissão para dispositivos ópticos ativos e passivos que operam nas regiões do espectro UV (ultravioleta) ao NIR (infravermelho próximo) e ideais para estruturas fotônicas ativas e passivas integradas, uma vez que não requerem tratamentos térmicos.

A rota híbrida sol-gel surgiu nos últimos 3 anos como uma rota química conveniente para obter materiais transparentes de HOI processáveis através de VPP. Rotas de síntese alternativas para materiais HOI não são inatamente compatíveis para VPP como a rota híbrida sol-gel, e muitas vezes sofrem de segregação de fase, produzindo materiais opacos. Essa rota de síntese permitiu a impressão de HOIs à base de silicato com boa qualidade óptica, que foram explorados na fabricação de estruturas ópticas passivas, como guias de onda. No entanto, essas matrizes não são boas candidatas para o desenvolvimento de dispositivos ópticos ativos, devido à sua baixa solubilidade de íons lantanídeos. Dessa maneira, há a necessidade de materiais HOI que sejam inerentemente compatíveis com a química dos lantanídeos para a fabricação de dispositivos ópticos ativos via VPP.

A este respeito, os materiais HOI a base de alumínio-fosfato (AIP) são candidatos promissores para a fabricação de dispositivos ópticos ativos. Compostos baseados em alumínio-fosfato possuem excelente solubilidade para os íons lantanídeos, impedindo a formação de *clusters* agrupamento e redução da fotoluminescência. A química do sol-gel AIP é desafiadora em comparação com a química bem estabelecida do sol-gel de silicato, uma vez que os precursores de fosfato e de alumínio para a rota sol-gel são muito reativos ou inertes. Até o momento, há pouca informação sobre a síntese de materiais transparentes e fotopolimerizáveis de AIP OIH.

O objetivo deste projeto de doutorado foi o desenvolvimento e caracterização estrutural de materiais híbridos à base de fosfato de alumínio obtidos a partir da rota sol-gel para a manufatura aditiva via VPP, com potencial aplicação na fabricação de novos dispositivos fotônicos ativos e passivos. Para tal, foi utilizado um sistema de VPP customizado operando sob condições de exposição intermitente, cujo princípio de funcionamento difere de plataformas comerciais. Foi desenvolvido um modelo matemático que descreve o perfil de exposição produzido pelo equipamento de VPP e os parâmetros operacionais para impressão dos materiais sintetizados, bem como suas cinéticas de fotopolimerização, foram estudados. Por fim, examinamos a homogeneidade óptica e a anisotropia de elementos manufaturados aditivamente a partir desses materiais.

Inicialmente, exploramos uma série de reagentes e protocolos de síntese para obter sóis fotopolimerizáveis à base de fosfato de alumínio adequados para VPP. A primeira série de materiais obtidos foi relatada no **Capítulo 1**, compreendendo materiais HOI formado por cadeias poliméricas de 2-hidroxietil metacrilato ligadas covalentemente a espécies de fosfato de alumínio, conforme revelado por RMN de estado sólido e espectroscopia de infravermelho. A conectividade entre os grupos

alumínio e fosfato foi investigada em profundidade por RMN de estado sólido, e os resultados demonstraram forte dependência com a relação alumínio/fósforo. Estruturalmente, essas unidades inorgânicas atuam como ligações cruzadas, resultando em uma estrutura inorgânica/orgânica altamente interconectada e interligada. Os materiais obtidos começam como soluções altamente estáveis que podem ser fotopolimerizadas para produzir materiais híbridos opticamente transparentes na faixa de 420 nm - 1100 nm, e com baixa retração volumétrica comparado a materiais do tipo metacrilato, tornando-os candidatos ideais para manufatura aditiva via VPP. No entanto, esses materiais apresentaram baixa transmitância na região do infravermelho próximo (NIR) devido ao alto teor orgânico dessas matrizes.

Esses materiais tiveram suas propriedades de transmissão melhoradas através da substituição do 2-hidroxietil metacrilato por um precursor de alcoxissilano, resultando em materiais híbridos de alumínio-fosfato-silicato, conforme reportado no **Capítulo 2**. De maneira similar, obtivemos soluções fotopolimerizáveis e estáveis, compatíveis com as tecnologias de VPP, resultando em materiais híbridos transparentes com alto teor de massa inorgânica (até 40% em massa) e melhor transmitância no NIR, conforme ilustrado na **Figure 70**.

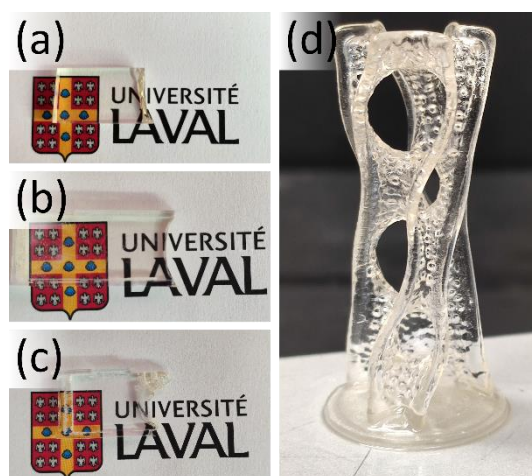


Figure 70. Monolitos polidos obtidos a partir da termopolimerização dos materiais de composição 30% TMSPM com razão Al:P de (a) 1:1, (b) 3:1, e (c) 1:3. Espessura entre 2 e 4 mm, com largura de 10 mm e comprimento de 15 a 30 mm. (d) Torre de Voroni impressa 3D (5 cm de altura) com o material 0% TMSPM Al:P = 1:1 (1% em massa de TPO).

A evolução estrutural com a concentração de Si para amostras com diferentes razões Al:P foi investigada por meio de RMN de estado sólido, microscopia eletrônica de varredura (MEV), e microscopia de força atômica com contraste de fase. Uma análise detalhada por meio de RMN de

estado sólido mostrou que esses materiais seguem o princípio de construção *build-up*, com espécies de fosfato de alumínio e cadeias de alcoxissilano atuando como blocos fundamentais. A razão Al:P determina a heterocondensação dos precursores de alumínio e fosfato e a estrutura das unidades de fosfato de alumínio resultantes. Essas estruturas se apresentaram como compostos lineares de fosfato de alumínio com natureza monomérica ou dimérica, dependendo da razão Al:P, conforme ilustrado na **Figure 71**. A estrutura dimérica favorece a homocondensação do alcoxissilano, resultando em redes inorgânicas separadas de silicato e fosfato de alumínio, enquanto as estruturas monoméricas permitem a heterocondensação Al-O-Si, resultando em uma rede inorgânica composta por unidades de fosfato de alumínio interligadas por cadeias de silicato. Estas características estruturais apresentam estes materiais como candidatos potenciais para imobilizar íons lantanídeos para o desenvolvimento de componentes ópticos ativos.

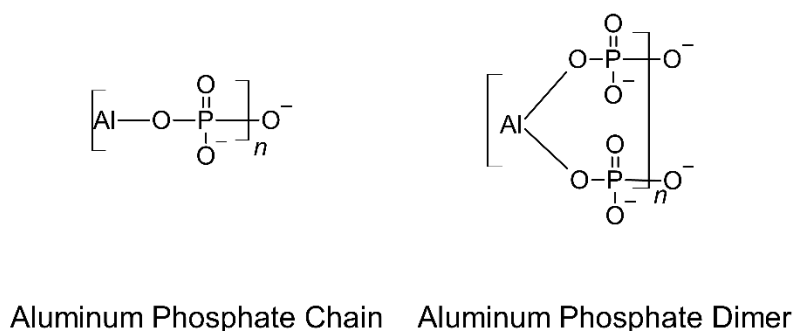


Figure 71. Estruturas lineares de alumino-fosfato do tipo monomérica e dimérica identificadas como bloco fundamentais compondo os materiais descritos no **Capítulo 2**.

No **Capítulo 3**, testamos um modelo matemático que descreve o perfil de exposição produzido pela impressora empregada neste trabalho, de maneira a permitir a correlação dos parâmetros de impressão medidos para nossos materiais com os de plataformas MA comerciais, conforme ilustrado na **Figure 72**. Observamos que o modelo possui a mesma dependência logarítmica da curva de trabalho de Jacobs (empregada em sistemas comerciais), com a adição de um fator que descreve a sobreposição de pulsos adjacentes, permitindo que os parâmetros de impressão medidos para nossas resinas em nossa plataforma customizada sejam extrapolados para outros equipamentos comerciais.

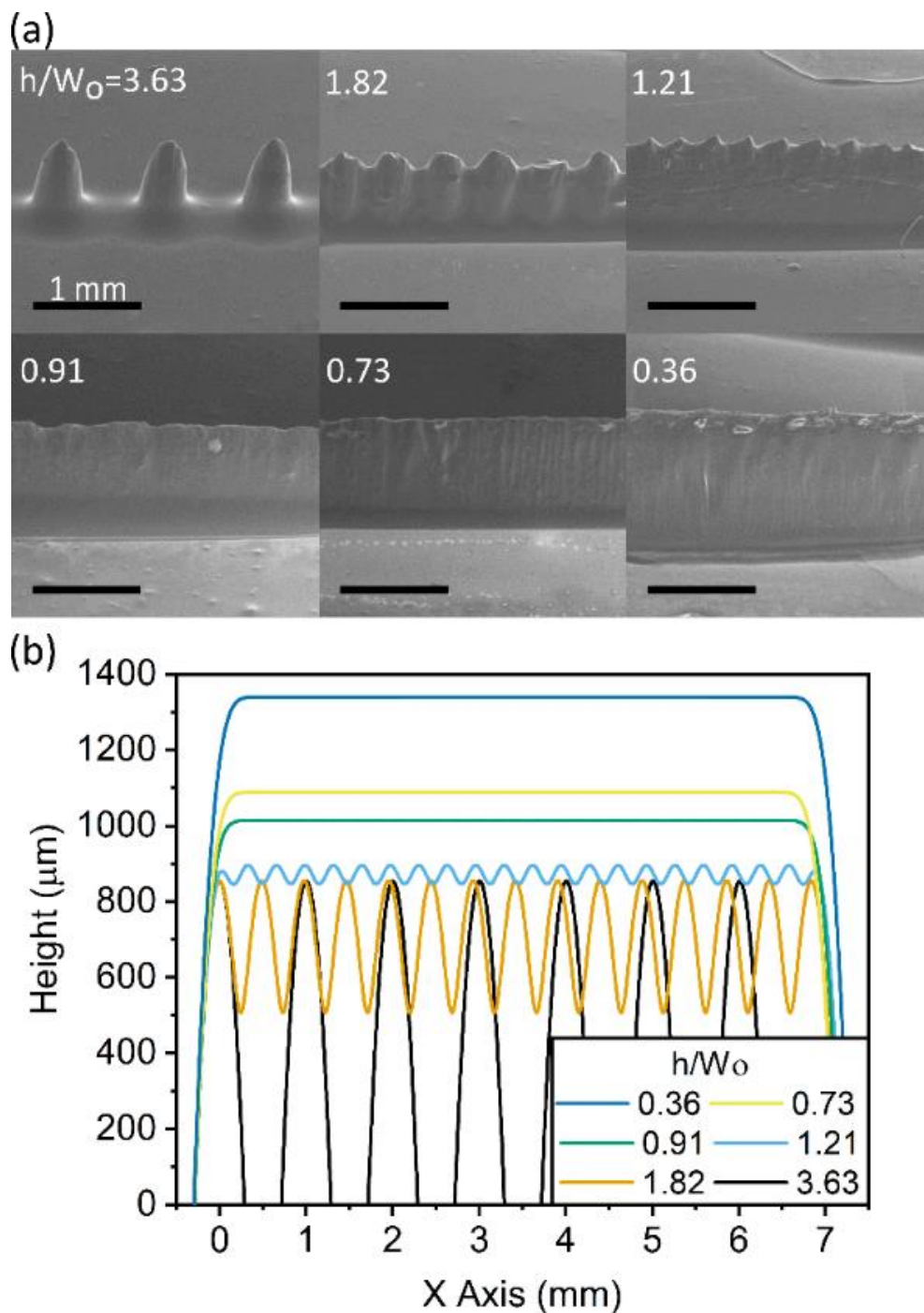


Figure 72. (a) Imagem de MEV de uma linha impressa 3D utilizando diferentes distâncias interpulso com um material de composição 0.73 % em massa de fotoiniciador e [PETA/BAPO]-[MPTMS-HAD] utilizando um laser de emissão em 360 nm ($\phi=550\pm 10\text{ }\mu\text{m}$), potência de 800 μW ($336.7\text{ mW}\cdot\text{cm}^{-2}$), e 100 ms de tempo de exposição. Escala de 1 mm; (b) Perfil topográfico de acordo com o modelo VPP-UVL-IE calculado a partir dos mesmos parâmetros experimentais.

No **Capítulo 4**, exploramos a manufatura aditiva das resinas de alumínio-fosfato-silicato estudadas no **Capítulo 2**. A evolução dos parâmetros de impressão 3D desses materiais (energia crítica e profundidade de penetração) e da cinética de fotopolimerização com intensidade de luz e silicato concentração foram estudados, conforme ilustrado na **Figure 73**. Além disso, usamos nossos dados experimentais para validar um modelo fotoquímico publicado na literatura descrevendo o processo VPP. O modelo prevê que $E_c \propto (k_t^{1/2}/k_p) \ln p_c$ and $D_p \propto \epsilon$, where k_t , k_p , p_c , and ϵ são a constante cinética de terminação bimolecular, constante cinética de propagação, conversão crítica e coeficiente de absorção no comprimento de onda do laser, respectivamente. Nosso estudo revela que tanto $E_c \propto (k_t^{1/2}/k_p)$ and $D_p \propto \epsilon$ as relações são verdadeiras e existe uma ligação entre a energia crítica e as constantes cinéticas que descrevem o processo de polimerização de um determinado material.

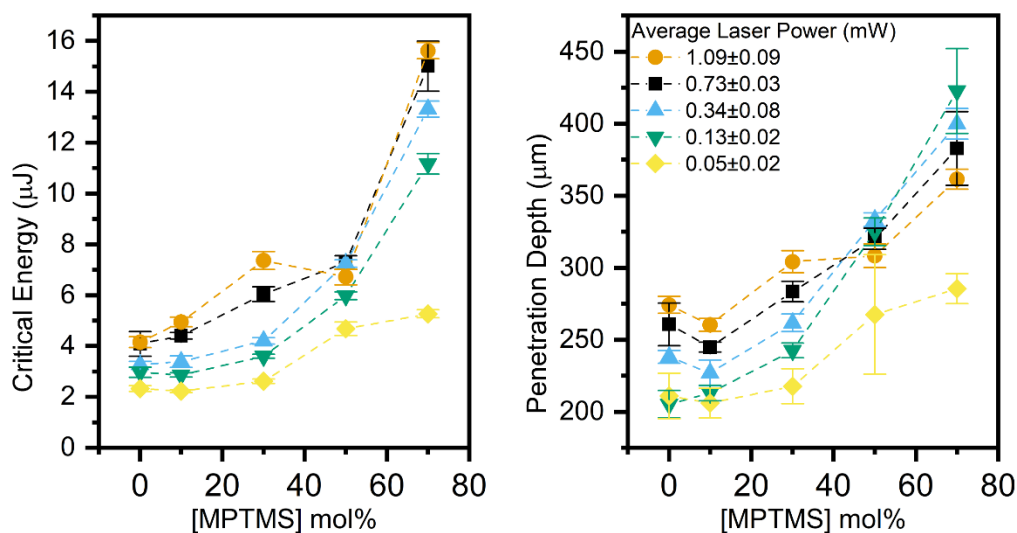


Figure 73. Energia crítica (a direita) e profundidade de penetração (a esquerda) em função da concentração de MPTMS medidas com potências de laser médio de 1.09, 0.73, 0.34, 0.13, e 0.05 mW.

Por fim, no **Capítulo 5**, estudamos a distribuição do índice de refração e a presença de anisotropias ópticas em linhas impressas em 3D fabricadas com uma das resinas de alumínio-fosfato-silicato estudadas no Capítulo 2. O mapeamento micro-Raman mostrou um gradiente de grau de polimerização presente nas linhas, onde menores conversões C=C foram alcançadas à medida que a intensidade da luz diminuiu (penetração mais profunda da luz e mais distante do centro do feixe), no entanto, esse gradiente não resultou em variações de índice de refração superiores ao limite de detecção do nosso procedimento de medição ($<10^{-4}$). Imagens de polarimetria revelaram a presença

de anisotropias ópticas nessas linhas, conforme ilustrado na **Figure 74**; no entanto, essas anisotropias não surgem devido ao alinhamento molecular, como mostrado pelo mapeamento micro-Raman polarizado, indicando que a birrefringência surge da tensão de cisalhamento perpendicular à direção da varredura do laser durante a impressão 3D, resultando em influxo de monômero em direção ao ponto de polimerização.

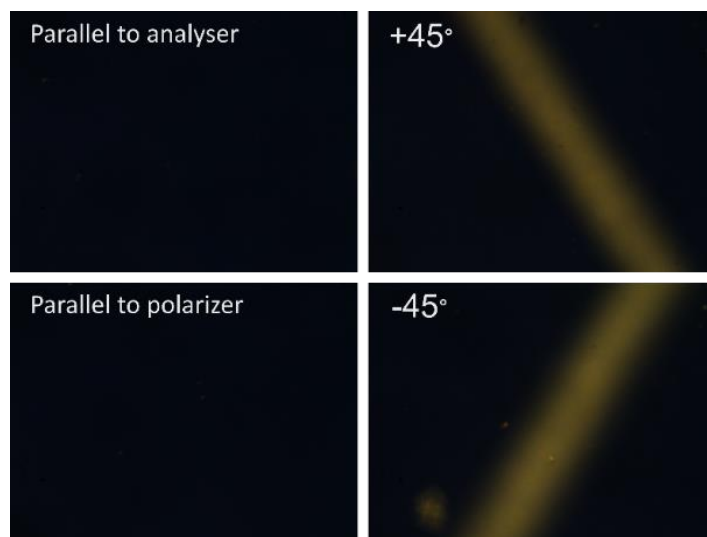


Figure 74. Imagens de polarimetria de uma linha impressa 3D e imersa óleo de mesmo índice de refração. Fotos adquiridas com a linha alinhada paralela, +45, -45, e perpendicular ao polarizador.

BIBLIOGRAPHIC REFERENCES

- [1] S. Mellor, L. Hao, and D. Zhang, "Additive manufacturing: A framework for implementation," *International Journal of Production Economics*, vol. 149, pp. 194–201, 2014, doi: 10.1016/j.ijpe.2013.07.008.
- [2] T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Q. Nguyen, and D. Hui, "Additive manufacturing (3D printing): A review of materials, methods, applications and challenges," *Composites Part B: Engineering*, vol. 143, no. December 2017, pp. 172–196, Jun. 2018, doi: 10.1016/j.compositesb.2018.02.012.
- [3] B. Bhushan and M. Caspers, "An overview of additive manufacturing (3D printing) for microfabrication," *Microsystem Technologies*, vol. 23, no. 4, pp. 1117–1124, 2017, doi: 10.1007/s00542-017-3342-8.
- [4] C. L. Weber *et al.*, "The Role of the National Science Foundation in the Origin and Evolution of Additive Manufacturing in the United States," 2013. [Online]. Available: <https://www.ida.org/idamedia/Corporate/Files/Publications/STIPubs/ida-p-5091.ashx>
- [5] A. Camposeo, L. Persano, M. Farsari, and D. Pisignano, "Additive Manufacturing: Applications and Directions in Photonics and Optoelectronics," *Advanced Optical Materials*, vol. 7, no. 1, 2019, doi: 10.1002/adom.201800419.
- [6] J. I. N. G. Y. Ang *et al.*, "3D printed low-loss THz waveguide based on Kagome photonic crystal structure," *Optic Express*, vol. 24, no. 20, pp. 22454–22460, 2016.
- [7] K. Cook *et al.*, "Step-index optical fiber drawn from 3D printed preforms," *Optics Letters*, vol. 41, no. 19, pp. 4554–4557, 2016, doi: 10.1364/OL.41.004554.
- [8] B. Lebeau and P. Innocenzi, "Hybrid materials for optics and photonics," *Chem. Soc. Rev.*, vol. 40, no. 2, p. 886, 2011, doi: 10.1039/c0cs00106f.
- [9] B. Yan, "Recent progress in photofunctional lanthanide hybrid materials," *RSC Advances*, vol. 2, no. 25, pp. 9304–9304, 2012, doi: 10.1039/c2ra20976d.
- [10] R. A. S. Ferreira, P. S. André, and L. D. Carlos, "Organic-inorganic hybrid materials towards passive and active architectures for the next generation of optical networks," *Optical Materials*, vol. 32, no. 11, pp. 1397–1409, 2010, doi: 10.1016/j.optmat.2010.06.019.
- [11] L. D. Carlos, R. A. S. Ferreira, V. de Zea Bermudez, B. Julián-López, and P. Escribano, "Progress on lanthanide-based organic–inorganic hybrid phosphors," *Chem. Soc. Rev.*, vol. 40, no. 2, pp. 536–549, 2011, doi: 10.1039/C0CS00069H.
- [12] I. Cooperstein *et al.*, "Hybrid Materials for Functional 3D Printing," *Advanced Materials Interfaces*, vol. 1800996, pp. 1–15, 2018, doi: 10.1002/admi.201800996.
- [13] P. Judeinstein and C. Sanchez, "Hybrid organic–inorganic materials: a land of multidisciplinary," *J. Mater. Chem.*, vol. 6, no. 4, pp. 511–525, 1996, doi: 10.1039/JM9960600511.
- [14] L. Nicole, C. Laberty-Robert, L. Rozes, and C. Sanchez, "Hybrid materials science: a promised land for the integrative design of multifunctional materials," *Nanoscale*, vol. 6, no. 12, pp. 6267–6292, 2014, doi: 10.1039/C4NR01788A.
- [15] C. Sanchez, G. J. de A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, and V. Cabuil, "Designed Hybrid Organic–Inorganic Nanocomposites from Functional Nanobuilding Blocks," *Chemistry of Materials*, vol. 13, no. 10, pp. 3061–3083, Oct. 2001, doi: 10.1021/cm011061e.
- [16] F. Ribot and C. Sanchez, "Organically Functionalized Metallic Oxo-Clusters: Structurally Well-Defined Nanobuilding Blocks for the Design of Hybrid Organic-Inorganic Materials," *Comments*

- on *Inorganic Chemistry*, vol. 20, no. 4–6, pp. 327–371, Jan. 1999, doi: 10.1080/02603599908021449.
- [17] I. Cooperstein, E. Shukrun, O. Press, A. Kamyshny, and S. Magdassi, “Additive Manufacturing of Transparent Silica Glass from Solutions,” *ACS Applied Materials and Interfaces*, vol. 10, no. 22, pp. 18879–18885, 2018, doi: 10.1021/acsami.8b03766.
 - [18] E. Shukrun, I. Cooperstein, and S. Magdassi, “3D-Printed Organic–Ceramic Complex Hybrid Structures with High Silica Content,” *Advanced Science*, vol. 5, no. 8, pp. 1–7, 2018, doi: 10.1002/advs.201800061.
 - [19] K. Arai, H. Namikawa, K. Kumata, T. Honda, Y. Ishii, and T. Handa, “Aluminum or phosphorus co-doping effects on the fluorescence and structural properties of neodymium-doped silica glass,” *Journal of Applied Physics*, vol. 59, no. 10, pp. 3430–3436, May 1986, doi: 10.1063/1.336810.
 - [20] N. O. Dantas, E. O. Serqueira, A. C. A. Silva, A. A. Andrade, and S. A. Lourenço, “High Quantum Efficiency of Nd³⁺ Ions in a Phosphate Glass System using the Judd–Ofelt Theory,” *Braz J Phys*, vol. 43, no. 4, pp. 230–238, Aug. 2013, doi: 10.1007/s13538-013-0145-y.
 - [21] J. Livage, P. Barboux, M. T. Vandenborre, C. Schmutz, and F. Taulelle, “Sol-gel synthesis of phosphates,” *Journal of Non-Crystalline Solids*, vol. 147–148, pp. 18–23, 1992.
 - [22] F. Babonneau, L. Coury, and J. Livage, “Aluminum sec-butoxide modified with ethylacetoacetate: An attractive precursor for the sol-gel synthesis of ceramics,” *Journal of Non-Crystalline Solids*, vol. 121, no. 1–3, pp. 153–157, May 1990, doi: 10.1016/0022-3093(90)90122-3.
 - [23] R. Lichtenberger, M. Puchberger, S. O. Baumann, and U. Schubert, “Modification of aluminum alkoxides with β -ketoesters: new insights into formation, structure and stability,” *Journal of Sol-Gel Science and Technology*, vol. 50, no. 2, pp. 130–140, May 2009, doi: 10.1007/s10971-008-1890-1.
 - [24] I. Gibson, D. Rosen, and B. Stucker, *Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing*, Second edi. Springer US, 2015. doi: 10.1520/F2792-12A.2.
 - [25] B. Redwood, F. Schöffner, and B. Garret, “The 3D Printing Handbook,” *3D Hubs*, p. 304, 2017.
 - [26] B. DeBoer, N. Nguyen, F. Diba, and A. Hosseini, “Additive, subtractive, and formative manufacturing of metal components: a life cycle assessment comparison,” *Int J Adv Manuf Technol*, vol. 115, no. 1–2, pp. 413–432, Jul. 2021, doi: 10.1007/s00170-021-07173-5.
 - [27] B. Bhushan and M. Caspers, “An overview of additive manufacturing (3D printing) for microfabrication,” *Microsystem Technologies*, vol. 23, no. 4, pp. 1117–1124, 2017, doi: 10.1007/s00542-017-3342-8.
 - [28] J. Butt, “Exploring the Interrelationship between Additive Manufacturing and Industry 4.0,” *Designs*, vol. 4, no. 2, Art. no. 2, Jun. 2020, doi: 10.3390/designs4020013.
 - [29] M. E. Hernandez Korner, M. P. Lambán, J. A. Albajez, J. Santolaria, L. del C. Ng Corrales, and J. Royo, “Systematic Literature Review: Integration of Additive Manufacturing and Industry 4.0,” *Metals*, vol. 10, no. 8, Art. no. 8, Aug. 2020, doi: 10.3390/met10081061.
 - [30] S. M. E. Sepasgozar, A. Shi, L. Yang, S. Shirowzhan, and D. J. Edwards, “Additive Manufacturing Applications for Industry 4.0: A Systematic Critical Review,” *Buildings*, vol. 10, no. 12, Art. no. 12, Dec. 2020, doi: 10.3390/buildings10120231.
 - [31] S. Mellor, L. Hao, and D. Zhang, “Additive manufacturing: A framework for implementation,” *International Journal of Production Economics*, vol. 149, pp. 194–201, 2014, doi: 10.1016/j.ijpe.2013.07.008.

- [32] W. Gao *et al.*, "The status, challenges, and future of additive manufacturing in engineering," *CAD Computer Aided Design*, vol. 69, pp. 65–89, 2015, doi: 10.1016/j.cad.2015.04.001.
- [33] P. Tack, J. Victor, P. Gemmel, and L. Annemans, "3D-printing techniques in a medical setting: A systematic literature review," *BioMedical Engineering Online*, vol. 15, no. 1, pp. 1–22, 2016, doi: 10.1186/s12938-016-0236-4.
- [34] J. M. Nadal-Serrano, A. Nadal-Serrano, and M. Lopez-Vallejo, "Democratizing science with the aid of parametric design and additive manufacturing: Design and fabrication of a versatile and low-cost optical instrument for scattering measurement," *PLoS ONE*, vol. 12, no. 11, pp. 1–18, 2017, doi: 10.1371/journal.pone.0187219.
- [35] J. Goole and K. Amighi, "3D printing in pharmaceuticals: A new tool for designing customized drug delivery systems," *International Journal of Pharmaceutics*, vol. 499, no. 1–2, pp. 376–394, 2016, doi: 10.1016/j.ijpharm.2015.12.071.
- [36] F. C. Godoi, S. Prakash, and B. R. Bhandari, "3d printing technologies applied for food design: Status and prospects," *Journal of Food Engineering*, vol. 179, pp. 44–54, 2016, doi: 10.1016/j.jfoodeng.2016.01.025.
- [37] M. LaMonica, "Additive Manufacturing: GE, the world's largest manufacturer, is on the verge of using 3-D printing to make jet parts," *MIT Technology Review*, vol. 116, no. 3, p. 59, 2014, doi: 10.1016/B978-0-08-096532-1.01000-1.
- [38] ASTM International, "F2792-12a - Standard Terminology for Additive Manufacturing Technologies," *Rapid Manufacturing Association*, pp. 10–12, 2013, doi: 10.1520/F2792-12A.2.
- [39] "Additive manufacturing - General principles - Fundamentals and vocabulary," ISO/ASTM, International standard ISO/ASTM 52900:2021(E), 2021. doi: 10.3403/30448424.
- [40] M. Ziaee and N. B. Crane, "Binder jetting: A review of process, materials, and methods," *Additive Manufacturing*, vol. 28, pp. 781–801, Aug. 2019, doi: 10.1016/j.addma.2019.05.031.
- [41] D.-G. Ahn, "Directed Energy Deposition (DED) Process: State of the Art," *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, vol. 8, no. 2, pp. 703–742, Mar. 2021, doi: 10.1007/s40684-020-00302-7.
- [42] A. Oleff, B. Küster, M. Stonis, and L. Overmeyer, "Process monitoring for material extrusion additive manufacturing: a state-of-the-art review," *Prog Addit Manuf*, vol. 6, no. 4, pp. 705–730, Dec. 2021, doi: 10.1007/s40964-021-00192-4.
- [43] J. Gonzalez-Gutierrez, S. Cano, S. Schuschnigg, C. Kukla, J. Sapkota, and C. Holzer, "Additive Manufacturing of Metallic and Ceramic Components by the Material Extrusion of Highly-Filled Polymers: A Review and Future Perspectives," *Materials*, vol. 11, no. 5, Art. no. 5, May 2018, doi: 10.3390/ma11050840.
- [44] R. Singh *et al.*, "Powder bed fusion process in additive manufacturing: An overview," *Materials Today: Proceedings*, vol. 26, pp. 3058–3070, Jan. 2020, doi: 10.1016/j.matpr.2020.02.635.
- [45] T. Özel, A. Altay, B. Kaftanoğlu, R. Leach, N. Senin, and A. Donmez, "Focus Variation Measurement and Prediction of Surface Texture Parameters Using Machine Learning in Laser Powder Bed Fusion," *Journal of Manufacturing Science and Engineering*, vol. 142, no. 1, Nov. 2019, doi: 10.1115/1.4045415.
- [46] O. Gülcan, K. Günaydın, and A. Tamer, "The State of the Art of Material Jetting—A Critical Review," *Polymers*, vol. 13, no. 16, Art. no. 16, Jan. 2021, doi: 10.3390/polym13162829.
- [47] B. Derby, "Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution," *Annual Review of Materials Research*, vol. 40, no. 1, pp. 395–414, Jun. 2010, doi: 10.1146/annurev-matsci-070909-104502.
- [48] J. Zhang and P. Xiao, "3D printing of photopolymers," *Polymer Chemistry*, vol. 9, no. 13. Royal Society of Chemistry, pp. 1530–1540, 2018. doi: 10.1039/c8py00157j.

- [49] R. Liska *et al.*, "Photopolymers for rapid prototyping," *Journal of Coatings Technology and Research*, vol. 4, no. 4, pp. 505–510, Nov. 2007, doi: 10.1007/s11998-007-9059-3.
- [50] M. Mao *et al.*, "The emerging frontiers and applications of high-resolution 3D printing," *Micromachines*, vol. 8, no. 4, pp. 1–20, 2017, doi: 10.3390/mi8040113.
- [51] M. Shah *et al.*, "Vat photopolymerization-based 3D printing of polymer nanocomposites: current trends and applications," *RSC Advances*, vol. 13, no. 2, pp. 1456–1496, 2023, doi: 10.1039/D2RA06522C.
- [52] Y. Zhu *et al.*, "Recent advancements and applications in 3D printing of functional optics," *Additive Manufacturing*, vol. 52, p. 102682, Apr. 2022, doi: 10.1016/j.addma.2022.102682.
- [53] Y. Cao *et al.*, "Polymer/glass hybrid DC-MZI thermal optical switch for 3D-integrated chips," *RSC Advances*, vol. 9, no. 19, pp. 10651–10656, 2019, doi: 10.1039/c9ra00037b.
- [54] R. Gvishi and I. Sokolov, "3D sol–gel printing and sol–gel bonding for fabrication of macro- and micro/nano-structured photonic devices," *Journal of Sol-Gel Science and Technology*, 2020, doi: 10.1007/s10971-020-05270-7.
- [55] T. Gissibl, S. Thiele, A. Herkommer, and H. Giessen, "Two-photon direct laser writing of ultracompact multi-lens objectives," *Nature Photonics*, vol. 10, no. 8, pp. 554–560, 2016, doi: 10.1038/nphoton.2016.121.
- [56] S. Juodkakis, "Manufacturing: 3D printed micro-optics," *Nature Photonics*, vol. 10, no. 8, pp. 499–501, 2016, doi: 10.1038/nphoton.2016.150.
- [57] N. Vaidya and O. Solgaard, "3D printed optics with nanometer scale surface roughness," *Microsyst Nanoeng*, vol. 4, no. 1, p. 18, Dec. 2018, doi: 10.1038/s41378-018-0015-4.
- [58] G. Berglund, A. Wisniowiecki, J. Gawedzinski, B. Applegate, and T. S. Tkaczyk, "Additive manufacturing for the development of optical/photonic systems and components," *Optica*, vol. 9, no. 6, p. 623, Jun. 2022, doi: 10.1364/OPTICA.451642.
- [59] A. L. S. Cruz *et al.*, "3D Printed Hollow Core Fiber with Negative Curvature for Terahertz Applications," *Journal of Microwaves, Optoelectronics and Electromagnetic Applications*, vol. 14, no. SI-1, pp. 45–53, 2015.
- [60] A. L. S. Cruz, C. M. B. Cordeiro, and M. A. R. Franco, "3D Printed Hollow-Core Terahertz Fibers," *Fibers*, vol. 6, no. 43, pp. 1–11, 2018, doi: 10.3390/fib6030043.
- [61] C. R. Tubío, J. A. Nóvoa, J. Martín, F. Guitián, J. R. Salgueiro, and A. Gil, "3D printing of Al₂O₃ photonic crystals for terahertz frequencies," *RSC Adv.*, vol. 6, no. 3, pp. 2450–2454, 2016, doi: 10.1039/C5RA22737B.
- [62] Q. Zhao *et al.*, "Optical fibers with special shaped cores drawn from 3D printed preforms," *Optik*, vol. 133, no. 19, pp. 60–65, Mar. 2017, doi: 10.1016/j.ijleo.2017.01.002.
- [63] K. Cook *et al.*, "Air-structured optical fiber drawn from a 3D-printed preform," *Optics Letters*, vol. 40, no. 17, pp. 3966–3969, 2015, doi: 10.1364/OL.40.003966.
- [64] Y. Chu *et al.*, "Silica optical fiber drawn from 3D printed preforms," *Opt. Lett., OL*, vol. 44, no. 21, pp. 5358–5361, Nov. 2019, doi: 10.1364/OL.44.005358.
- [65] D. Zhu, J. Zhang, Q. Xu, and Y. Li, "3D Printing of Customized Aspheric Lenses for Imaging," *Polymers*, vol. 13, no. 20, p. 3477, Oct. 2021, doi: 10.3390/polym13203477.
- [66] U. Blessing and K. Blessing, "Device for directing light beams, illustration device, method for producing a device and an illustration device," US20160341851A1, Nov. 24, 2016 Accessed: Jan. 31, 2023. [Online]. Available: <https://patents.google.com/patent/US20160341851A1/en?q=Luxexcel&oq=Luxexcel+>
- [67] K. Blessing and R. van de Vrie, "Print head, upgrade kit for a conventional inkjet printer, printer and method for printing optical structures," US9592690B2, Mar. 14, 2017 Accessed: Jan. 31,

2023. [Online]. Available: <https://patents.google.com/patent/US9592690B2/en?q=Luxexcel&oq=Luxexcel+>
- [68] R. van de Vrie, J. Biskop, and R. Blomaard, "Device for printing a three-dimensional structure," US20160271869A1, Sep. 22, 2016 Accessed: Jan. 31, 2023. [Online]. Available: <https://patents.google.com/patent/US20160271869A1/en?q=Luxexcel&oq=Luxexcel+>
- [69] R. van de Vrie and J. Biskop, "Method for printing a three-dimensional structure, method for controlling a print head and printed article," US9463597B2, Oct. 11, 2016 Accessed: Jan. 31, 2023. [Online]. Available: <https://patents.google.com/patent/US9463597B2/en?q=Luxexcel&oq=Luxexcel+>
- [70] "Applications in Microoptics, Optoelectronics & Photonics Packaging, Mastering, Biomedical Engineering." <https://multiphoton.de/technology/application-examples> (accessed Mar. 13, 2023).
- [71] "Wide range of applications in research, prototyping and production processes." <https://www.nanoscribe.com/en/applications/> (accessed Mar. 13, 2023).
- [72] M. Et, "Production of 3D Free-Form waveguide structures," US 10343332 B2, 2019
- [73] M. Ali, F. Alam, Y. F. Fah, O. Shiryayev, N. Vahdati, and H. Butt, "4D printed thermochromic Fresnel lenses for sensing applications," *Composites Part B: Engineering*, vol. 230, p. 109514, Feb. 2022, doi: 10.1016/j.compositesb.2021.109514.
- [74] M. Ali, F. Alam, and H. Butt, "Fabrication of 5D Fresnel Lenses via Additive Manufacturing," *ACS Mater. Au*, vol. 2, no. 5, pp. 602–613, Sep. 2022, doi: 10.1021/acsmaterialsau.2c00026.
- [75] M. Ali, F. Alam, N. Vahdati, and H. Butt, "3D-Printed Holographic Fresnel Lenses," *Advanced Engineering Materials*, vol. 24, no. 9, p. 2101641, Sep. 2022, doi: 10.1002/adem.202101641.
- [76] M. Hossain and M. Gu, "Fabrication methods of 3D periodic metallic nano / microstructures for photonics applications," *Laser and Photonics Reviews*, vol. 8, no. 2, pp. 233–249, 2013, doi: 10.1002/lpor.201300052.
- [77] Y. L. Kong *et al.*, "3D Printed Quantum Dot Light-Emitting Diodes," *Nano Letters*, vol. 14, no. 12, pp. 7017–7023, 2014, doi: 10.1021/nl5033292.
- [78] R. Dangel, B. Offrein, U. Troppenz, M. Moehrle, W. Freude, and C. Koos, "In situ 3D nanoprinting of free-form coupling elements for hybrid photonic integration," *Nature Photonics*, vol. 12, no. April, 2018, doi: 10.1038/s41566-018-0133-4.
- [79] T. Pereira, S. Rusinkiewicz, W. Matusik, and M. Csail, "Computational Light Routing : 3D Printed Optical Fibers for Sensing and Display," *ACM Transactions on Graphics*, vol. 33, no. 3, p. 24:1–24:13, 2014, doi: 10.1145/2602140.
- [80] S. Korobogatiy, "3D printed hollow core terahertz Bragg waveguides with defect layers for surface sensing applications," *Optic Express*, vol. 25, no. 4, pp. 309–322, 2017.
- [81] R. Wang, W. Yang, P. Zhu, S. Gao, B. Li, and Q. Li, "Creation of 3D terahertz photonic crystals by the direct writing technique with a TiO₂sol-gel ink," *Journal of the American Ceramic Society*, vol. 101, no. 5, pp. 1967–1973, 2018, doi: 10.1111/jace.15347.
- [82] Y. Liu *et al.*, "Structural color three-dimensional printing by shrinking photonic crystals," *Nat Commun*, vol. 10, no. 1, p. 4340, Dec. 2019, doi: 10.1038/s41467-019-12360-w.
- [83] F. Kotz *et al.*, "Liquid Glass: A Facile Soft Replication Method for Structuring Glass," *Advanced Materials*, vol. 28, pp. 4646–4650, 2016, doi: 10.1002/adma.201506089.
- [84] C. Xin, Z. Li, L. Hao, and Y. Li, "A comprehensive review on additive manufacturing of glass: Recent progress and future outlook," *Materials & Design*, vol. 227, p. 111736, Mar. 2023, doi: 10.1016/j.matdes.2023.111736.
- [85] J. Klein *et al.*, "Additive Manufacturing of Optically Transparent Glass," *3D Printing and Additive Manufacturing*, vol. 2, no. 3, pp. 92–105, 2015, doi: 10.1089/3dp.2015.0021.

- [86] S. Klein *et al.*, “3D printing of transparent glass,” *International Conference on Digital Printing Technologies*, pp. 336–337, 2012.
- [87] P.-T. Brun *et al.*, “The molten glass sewing machine,” *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 375, no. 2093, pp. 20160156–20160156, 2017, doi: 10.1098/rsta.2016.0156.
- [88] J. Luo, H. Pan, and E. C. Kinzel, “Additive Manufacturing of Glass,” *Journal of Manufacturing Science and Engineering*, vol. 136, no. 6, pp. 061024–061024, 2014, doi: 10.1115/1.4028531.
- [89] J. Luo *et al.*, “Additive manufacturing of glass for optical applications,” in *Proceedings of SPIE*, 2016, vol. Proc. SPIE, no. April 2016, p. 97380Y/1-97380Y/9. doi: 10.1117/12.2218137.
- [90] R. F. Shepherd *et al.*, “Stop-flow lithography of colloidal, glass, and silicon microcomponents,” *Advanced Materials*, vol. 20, no. 24, pp. 4734–4739, 2008, doi: 10.1002/adma.200801090.
- [91] G. Marchelli, R. Prabhakar, D. Storti, and M. Ganter, “The guide to glass 3D printing: developments, methods, diagnostics and results,” *Rapid Prototyping Journal*, vol. 17, no. 3, pp. 187–194, 2011, doi: 10.1108/13552541111124761.
- [92] J. F. Destino *et al.*, “3D Printed Optical Quality Silica and Silica-Titania Glasses from Sol-Gel Feedstocks,” *Advanced Materials Technologies*, vol. 1700323, pp. 1–10, 2018, doi: 10.1002/admt.201700323.
- [93] R. M. Zaki *et al.*, “Direct 3D-printing of phosphate glass by fused deposition modeling,” *Materials & Design*, vol. 194, p. 108957, Sep. 2020, doi: 10.1016/j.matdes.2020.108957.
- [94] S. Parola, B. Julián-López, L. D. Carlos, and C. Sanchez, “Optical Properties of Hybrid Organic-Inorganic Materials and their Applications,” *Advanced Functional Materials*, vol. 26, no. 36, pp. 6506–6544, Sep. 2016, doi: 10.1002/adfm.201602730.
- [95] M. Malinauskas *et al.*, “Femtosecond laser polymerization of hybrid/integrated micro-optical elements and their characterization,” *J. Opt.*, vol. 12, no. 12, p. 124010, Nov. 2010, doi: 10.1088/2040-8978/12/12/124010.
- [96] P. Wachholz, J. Wolf, S. Marx, D. Weber, J. Klein, and H. Schröder, “Novel technology for dispensing liquid polymers of a wide viscosity range on a picoliter scale for photonic applications,” in *Optical Interconnects XX*, Feb. 2020, vol. 11286, pp. 131–140. doi: 10.1117/12.2550566.
- [97] L. Jacot-Descombes *et al.*, “Organic-inorganic-hybrid-polymer microlens arrays with tailored optical characteristics and multi-focal properties,” *Opt. Express*, vol. 23, no. 19, p. 25365, Sep. 2015, doi: 10.1364/OE.23.025365.
- [98] J. Y. Kim, C. Martin-Olmos, N. S. Baek, and J. Brugger, “Simple and easily controllable parabolic-shaped microlenses printed on polymeric mesas,” *J. Mater. Chem. C*, vol. 1, no. 11, pp. 2152–2157, Feb. 2013, doi: 10.1039/C3TC00632H.
- [99] L. Jacot-Descombes, M. R. Gullo, V. J. Cadarso, and J. Brugger, “Fabrication of epoxy spherical microstructures by controlled drop-on-demand inkjet printing,” *J. Micromech. Microeng.*, vol. 22, no. 7, p. 074012, Jun. 2012, doi: 10.1088/0960-1317/22/7/074012.
- [100] D. J. Hayes, “Method for producing micro-optical components,” US5498444A, Mar. 12, 1996 Accessed: Mar. 17, 2023. [Online]. Available: <https://patents.google.com/patent/US5498444/en>
- [101] J. Y. Kim, K. Pfeiffer, A. Voigt, G. Gruetzner, and J. Brugger, “Directly fabricated multi-scale microlens arrays on a hydrophobic flat surface by a simple ink-jet printing technique,” *J. Mater. Chem.*, vol. 22, no. 7, pp. 3053–3058, Jan. 2012, doi: 10.1039/C2JM15576A.
- [102] A. Voigt *et al.*, “New inks for the direct drop-on-demand fabrication of polymer lenses,” *Microelectronic Engineering*, vol. 88, no. 8, pp. 2174–2179, Aug. 2011, doi: 10.1016/j.mee.2010.12.004.

- [103] J. Y. Kim *et al.*, “Hybrid polymer microlens arrays with high numerical apertures fabricated using simple ink-jet printing technique,” *Opt. Mater. Express, OME*, vol. 1, no. 2, pp. 259–269, Jun. 2011, doi: 10.1364/OME.1.000259.
- [104] R. Magazine, B. van Bochove, S. Borandeh, and J. Seppälä, “3D inkjet-printing of photo-crosslinkable resins for microlens fabrication,” *Additive Manufacturing*, vol. 50, p. 102534, Feb. 2022, doi: 10.1016/j.addma.2021.102534.
- [105] A. Žukauskas, M. Malinauskas, C. Reinhardt, B. N. Chichkov, and R. Gadonas, “Closely packed hexagonal conical microlens array fabricated by direct laser photopolymerization,” *Appl. Opt., AO*, vol. 51, no. 21, pp. 4995–5003, Jul. 2012, doi: 10.1364/AO.51.004995.
- [106] B. Sanchez-Padilla *et al.*, “Wrinkled axicons: shaping light from cusps,” *Opt. Express*, vol. 24, no. 21, p. 24075, Oct. 2016, doi: 10.1364/OE.24.024075.
- [107] T. Gissibl, S. Thiele, A. Herkommer, and H. Giessen, “Sub-micrometre accurate free-form optics by three-dimensional printing on single-mode fibres,” *Nat Commun*, vol. 7, no. 1, Art. no. 1, Jun. 2016, doi: 10.1038/ncomms11763.
- [108] S. Steenhusen, F. Burmeister, H.-C. Eckstein, and R. Houbertz, “Two-photon polymerization of hybrid polymers for applications in micro-optics,” presented at the SPIE LASE, San Francisco, California, United States, Mar. 2015, p. 93530K. doi: 10.1117/12.2079277.
- [109] S. Steenhusen, S. Hasselmann, and G. Domann, “Strategies for rapid and reliable fabrication of microoptical structures using two-photon polymerization,” in *Advanced Fabrication Technologies for Micro/Nano Optics and Photonics X*, Feb. 2017, vol. 10115, pp. 128–136. doi: 10.1117/12.2252913.
- [110] A. K. Petrov *et al.*, “Polymer X-ray refractive nano-lenses fabricated by additive technology,” *Opt Express*, vol. 25, no. 13, pp. 14173–14181, Jun. 2017, doi: 10.1364/OE.25.014173.
- [111] E. Johlin, S. A. Mann, S. Kasture, A. F. Koenderink, and E. C. Garnett, “Broadband highly directive 3D nanophotonic lenses,” *Nat Commun*, vol. 9, no. 1, Art. no. 1, Nov. 2018, doi: 10.1038/s41467-018-07104-1.
- [112] B. Stender, F. Hilbert, Y. Dupuis, A. Krupp, W. Mantei, and R. Houbertz, “Manufacturing strategies for scalable high-precision 3D printing of structures from the micro to the macro range,” *Advanced Optical Technologies*, vol. 8, pp. 225–231, Jun. 2019, doi: 10.1515/aot-2019-0022.
- [113] E. Brasselet, M. Malinauskas, A. Žukauskas, and S. Juodkasis, “Photopolymerized microscopic vortex beam generators: Precise delivery of optical orbital angular momentum,” *Appl. Phys. Lett.*, vol. 97, no. 21, p. 211108, Nov. 2010, doi: 10.1063/1.3517519.
- [114] A. Žukauskas, M. Malinauskas, and E. Brasselet, “Monolithic generators of pseudo-nondiffracting optical vortex beams at the microscale,” *Appl. Phys. Lett.*, vol. 103, no. 18, p. 181122, Oct. 2013, doi: 10.1063/1.4828662.
- [115] S. Krivec *et al.*, “Silica-Based, Organically Modified Host Material for Waveguide Structuring by Two-Photon-Induced Photopolymerization,” *Advanced Functional Materials*, vol. 20, no. 5, pp. 811–819, 2010, doi: 10.1002/adfm.200901790.
- [116] H. Segawa, K. Yoshida, T. Kondo, S. Matsuo, and H. Misawa, “Fabrication of Photonic Crystal Structures by Femtosecond Laser-Induced Photopolymerization of Organic-Inorganic Film,” *Journal of Sol-Gel Science and Technology*, vol. 26, no. 1, pp. 1023–1027, Jan. 2003, doi: 10.1023/A:1020729917721.
- [117] A. Ovsianikov *et al.*, “Ultra-Low Shrinkage Hybrid Photosensitive Material for Two-Photon Polymerization Microfabrication,” *ACS Nano*, vol. 2, no. 11, pp. 2257–2262, Nov. 2008, doi: 10.1021/nn800451w.

- [118] J. Serbin *et al.*, "Femtosecond laser-induced two-photon polymerization of inorganic–organic hybrid materials for applications in photonics," *Opt. Lett.*, vol. 28, no. 5, p. 301, Mar. 2003, doi: 10.1364/OL.28.000301.
- [119] J. Li, B. Jia, and M. Gu, "Engineering stop gaps of inorganic-organic polymeric 3D woodpile photonic crystals with post-thermal treatment," *Opt. Express*, OE, vol. 16, no. 24, pp. 20073–20080, Nov. 2008, doi: 10.1364/OE.16.020073.
- [120] Q. Sun, S. Juodkasis, N. Murazawa, V. Mizeikis, and H. Misawa, "Femtosecond laser photopolymerization of photonic and free-movable microstructures in sol-gel hybrid resist," presented at the MOEMS-MEMS, San Francisco, California, Feb. 2010, p. 75910K. doi: 10.1117/12.840657.
- [121] C.-L. Tai *et al.*, "Ultrastable, Deformable, and Stretchable Luminescent Organic–Inorganic Perovskite Nanocrystal–Polymer Composites for 3D Printing and White Light-Emitting Diodes," *ACS Applied Materials & Interfaces*, Jul. 2019, doi: 10.1021/acsami.9b06248.
- [122] C. Zhou *et al.*, "3D Printed Smart Windows for Adaptive Solar Modulations," *Adv. Optical Mater.*, vol. 8, no. 11, p. 2000013, Jun. 2020, doi: 10.1002/adom.202000013.
- [123] M. Faustini, D. Grosso, C. Boissière, R. Backov, and C. Sanchez, "Integrative sol–gel chemistry: a nanofoundry for materials science," *Journal of Sol-Gel Science and Technology*, vol. 70, no. 2, pp. 216–226, May 2014, doi: 10.1007/s10971-014-3321-9.
- [124] D. G. Moore, L. Barbera, K. Masania, and A. R. Studart, "Three-dimensional printing of multicomponent glasses using phase-separating resins," *Nature Materials*, vol. 19, no. 2, Art. no. 2, Feb. 2020, doi: 10.1038/s41563-019-0525-y.
- [125] Z. Li *et al.*, "Additive manufacturing of lightweight and high-strength polymer-derived SiOC ceramics," *Virtual and Physical Prototyping*, vol. 15, no. 2, pp. 163–177, Apr. 2020, doi: 10.1080/17452759.2019.1710919.
- [126] D. J. Lorang, D. Tanaka, C. M. Spadaccini, K. A. Rose, N. J. Cherepy, and J. A. Lewis, "Photocurable liquid core-fugitive shell printing of optical waveguides," *Advanced Materials*, vol. 23, no. 43, pp. 5055–5058, 2011, doi: 10.1002/adma.201102411.
- [127] A. Chiappone *et al.*, "3D Printed PEG-Based Hybrid Nanocomposites Obtained by Sol–Gel Technique," *ACS Applied Materials & Interfaces*, vol. 8, no. 8, pp. 5627–5633, Mar. 2016, doi: 10.1021/acsami.5b12578.
- [128] C. Echalié *et al.*, "Modular bioink for 3D printing of biocompatible hydrogels: sol–gel polymerization of hybrid peptides and polymers," *RSC Adv.*, vol. 7, no. 20, pp. 12231–12235, 2017, doi: 10.1039/C6RA28540F.
- [129] E. Stankevicius *et al.*, "Fabrication of micro-tube arrays in photopolymer SZ2080 by using three different methods of a direct laser polymerization technique," *J. Micromech. Microeng.*, vol. 22, no. 6, p. 065022, May 2012, doi: 10.1088/0960-1317/22/6/065022.
- [130] D. T. Pham and C. Ji, "A study of recoating in stereolithography," *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, vol. 217, no. 1, pp. 105–118, 2003, doi: 10.1243/095440603762554659.
- [131] K. Renap and J. P. Kruth, "Recoating issues in stereolithography," *Rapid Prototyping Journal*, vol. 1, no. 3, pp. 4–16, 1995, doi: 10.1108/13552549510094223.
- [132] D. T. Pham and C. Ji, "A study of recoating in stereolithography," *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, vol. 217, no. 1, pp. 105–118, 2003, doi: 10.1243/095440603762554659.
- [133] J. Bachmann *et al.*, "Cavity vat photopolymerisation for additive manufacturing of polymer-composite 3D objects," *Commun Mater*, vol. 2, no. 1, Art. no. 1, Oct. 2021, doi: 10.1038/s43246-021-00211-5.

- [134] P. F. Jacobs, *Rapid Prototyping & Manufacturing: Fundamentals of StereoLithography*. American Society of Mechanical Engineers, 1992, p. 369.
- [135] Jacobs P.F., *Stereolithography and other RP&M Technologies: from Rapid Prototyping to Rapid Tooling*. American Society of Mechanical Engineers, 1995.
- [136] J. Bennett, "Measuring UV curing parameters of commercial photopolymers used in additive manufacturing," *Additive Manufacturing*, vol. 18, pp. 203–212, 2017, doi: 10.1016/j.addma.2017.10.009.
- [137] T. F. Irzhak and V. I. Irzhak, "Critical conversion in polymerization processes," *Russ. Chem. Rev.*, vol. 79, no. 10, pp. 921–944, Dec. 2010, doi: 10.1070/RC2010v079n10ABEH004155.
- [138] V. Irzhak, "Methods of description of the polycondensation kinetics and the structures of the polymers formed," *Russian Chemical Reviews*, vol. 66, p. 541, Oct. 2007, doi: 10.1070/RC1997v066n06ABEH000346.
- [139] A. C. Uzcategui, A. Muralidharan, V. L. Ferguson, S. J. Bryant, and R. R. McLeod, "Understanding and Improving Mechanical Properties in 3D printed Parts Using a Dual-Cure Acrylate-Based Resin for Stereolithography," *Advanced Engineering Materials*, vol. 20, no. 12, p. 1800876, 2018, doi: 10.1002/adem.201800876.
- [140] Y. Abouliatim, T. Chartier, P. Abelard, C. Chaput, and C. Delage, "Optical characterization of stereolithography alumina suspensions using the Kubelka–Munk model," *Journal of the European Ceramic Society*, vol. 29, no. 5, pp. 919–924, Mar. 2009, doi: 10.1016/j.jeurceramsoc.2008.07.008.
- [141] V. Tomeckova and J. W. Halloran, "Cure depth for photopolymerization of ceramic suspensions," *Journal of the European Ceramic Society*, vol. 30, no. 15, pp. 3023–3033, 2010, doi: 10.1016/j.jeurceramsoc.2010.06.004.
- [142] V. Tomeckova and J. W. Halloran, "Predictive models for the photopolymerization of ceramic suspensions," *Journal of the European Ceramic Society*, vol. 30, no. 14, pp. 2833–2840, Oct. 2010, doi: 10.1016/j.jeurceramsoc.2010.01.027.
- [143] J. Tarabeux, V. Pateloup, P. Michaud, and T. Chartier, "Development of a numerical simulation model for predicting the curing of ceramic systems in the stereolithography process," *Journal of the European Ceramic Society*, vol. 38, no. 11, pp. 4089–4098, Sep. 2018, doi: 10.1016/j.jeurceramsoc.2018.03.052.
- [144] V. Tomeckova and J. W. Halloran, "Critical energy for photopolymerization of ceramic suspensions in acrylate monomers," *Journal of the European Ceramic Society*, vol. 30, no. 16, pp. 3273–3282, 2010, doi: 10.1016/j.jeurceramsoc.2010.08.003.
- [145] H. Li, Y. Qi, and J. T. Sheridan, "Three-dimensional extended nonlocal photopolymerization driven diffusion model Part II Photopolymerization and model development," *J. Opt. Soc. Am. B*, vol. 31, no. 11, p. 2648, Nov. 2014, doi: 10.1364/JOSAB.31.002648.
- [146] A. S. Jariwala *et al.*, "Modeling effects of oxygen inhibition in mask-based stereolithography," *Rapid Prototyping Journal*, vol. 17, no. 3, pp. 168–175, Apr. 2011, doi: 10.1108/13552541111124734.
- [147] M. M. Emami and D. W. Rosen, "An Improved Vat Photopolymerization Cure Model Demonstrates Photobleaching Effects," in *Solid Freeform Fabrication 2018: Proceedings of the 29th Annual International*, pp. 1940–1952. doi: <http://dx.doi.org/10.26153/tsw/17195>.
- [148] N. B. Cramer, C. P. O'Brien, and C. N. Bowman, "Mechanisms, polymerization rate scaling, and oxygen inhibition with an ultra-rapid monovinyl urethane acrylate," *Polymer*, vol. 49, no. 22, pp. 4756–4761, Oct. 2008, doi: 10.1016/j.polymer.2008.08.051.
- [149] Y. Tang, C. Henderson, J. Muzzy, and D. W. Rosen, "Stereolithography cure modelling and simulation," *IJMPT*, vol. 21, no. 4, p. 255, 2004, doi: 10.1504/IJMPT.2004.004941.

- [150] M. B. Belgacem, S. Kamoun, M. Gargouri, K. D. H. Dorkenoo, A. Barsella, and L. Mager, "Light induced self-written waveguides interactions in photopolymer media," *Opt. Express, OE*, vol. 23, no. 16, pp. 20841–20848, Aug. 2015, doi: 10.1364/OE.23.020841.
- [151] J. E. Elliott and C. N. Bowman, "Kinetics of Primary Cyclization Reactions in Cross-Linked Polymers: An Analytical and Numerical Approach to Heterogeneity in Network Formation," *Macromolecules*, vol. 32, no. 25, pp. 8621–8628, Dec. 1999, doi: 10.1021/ma990797i.
- [152] J. E. Elliott, L. G. Lovell, and C. N. Bowman, "Primary cyclization in the polymerization of bis-GMA and TEGDMA: a modeling approach to understanding the cure of dental resins," *Dental Materials*, vol. 17, no. 3, pp. 221–229, May 2001, doi: 10.1016/S0109-5641(00)00075-0.
- [153] J. W. Stansbury, "Cyclopolymerizable Monomers for Use in Dental Resin Composites," *J Dent Res*, vol. 69, no. 3, pp. 844–848, Mar. 1990, doi: 10.1177/00220345900690030201.
- [154] W. V. Camp, H. Gao, F. E. D. Prez, and K. Matyjaszewski, "Effect of crosslinker multiplicity on the gel point in ATRP," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 48, no. 9, pp. 2016–2023, 2010, doi: <https://doi.org/10.1002/pola.23970>.
- [155] G. A. O'Neil, M. B. Wisnudel, and J. M. Torkelson, "A Critical Experimental Examination of the Gel Effect in Free Radical Polymerization: Do Entanglements Cause Autoacceleration?," *Macromolecules*, vol. 29, no. 23, pp. 7477–7490, Jan. 1996, doi: 10.1021/ma9606263.
- [156] J. H. Lee, R. K. Prud'homme, and I. A. Aksay, "Cure depth in photopolymerization: Experiments and theory," *Journal of Materials Research*, vol. 16, no. 12, pp. 3536–3544, 2001, doi: 10.1557/JMR.2001.0485.
- [157] N. B. Cramer, C. P. O'Brien, and C. N. Bowman, "Mechanisms, polymerization rate scaling, and oxygen inhibition with an ultra-rapid monovinyl urethane acrylate," *Polymer*, vol. 49, no. 22, pp. 4756–4761, Oct. 2008, doi: 10.1016/j.polymer.2008.08.051.
- [158] J. W. Wydra, N. B. Cramer, J. W. Stansbury, and C. N. Bowman, "The reciprocity law concerning light dose relationships applied to BisGMA/TEGDMA photopolymers: Theoretical analysis and experimental characterization," *Dental Materials*, vol. 30, no. 6, pp. 605–612, Jun. 2014, doi: 10.1016/j.dental.2014.02.021.
- [159] W. Schnabel, *Polymers and Light*. Wiley, 2007, p. 382. doi: 10.1002/9783527611027.
- [160] J. P. Fouassier and J. Lalevée, *Photoinitiators for Polymer Synthesis*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2012, p. 490. doi: 10.1002/9783527648245.
- [161] J. P. Fouassier, X. Allonas, J. Laleve, and C. Dietlin, "Photoinitiators for Free Radical Polymerization Reactions," in *Photochemistry and Photophysics of Polymer Materials*, Hoboken, NJ, USA: John Wiley & Sons, Inc., 2010, pp. 351–419. doi: 10.1002/9780470594179.ch10.
- [162] E. Andrzejewska, "Photopolymerization kinetics of multifunctional monomers," *Progress in Polymer Science*, vol. 26, no. 4, pp. 605–665, May 2001, doi: 10.1016/S0079-6700(01)00004-1.
- [163] J. V. Crivello and E. Reichmanis, "Photopolymer materials and processes for advanced technologies," *Chemistry of Materials*, vol. 26, no. 1, pp. 533–548, 2014, doi: 10.1021/cm402262g.
- [164] C. Decker and A. D. Jenkins, "Kinetic approach of oxygen inhibition in ultraviolet- and laser-induced polymerizations," *Macromolecules*, vol. 18, no. 6, pp. 1241–1244, Nov. 1985, doi: 10.1021/ma00148a034.
- [165] J. Lalevée, H. Mokbel, and J.-P. Fouassier, "Recent Developments of Versatile Photoinitiating Systems for Cationic Ring Opening Polymerization Operating at Any Wavelengths and under Low Light Intensity Sources," *Molecules*, vol. 20, no. 4, pp. 7201–7221, Apr. 2015, doi: 10.3390/molecules20047201.

- [166] M. D. Goodner and C. N. Bowman, "Modeling Primary Radical Termination and Its Effects on Autoacceleration in Photopolymerization Kinetics," *Macromolecules*, vol. 32, no. 20, pp. 6552–6559, Oct. 1999, doi: 10.1021/ma9901947.
- [167] J. V. Crivello, S. Holdcroft, and A. S. Hay, "Synergistic Effects in Hybrid Free Radical/Cationic Photopolymerizations," *American Chemical Society, Polymer Preprints, Division of Polymer Chemistry*, vol. 49, no. 1, pp. 511–512, 2008, doi: 10.1002/pola.
- [168] C. Decker, T. Nguyen Thi Viet, D. Decker, and E. Weber-Koehl, "UV-radiation curing of acrylate/epoxide systems," *Polymer*, vol. 42, no. 13, pp. 5531–5541, Jun. 2001, doi: 10.1016/S0032-3861(01)00065-9.
- [169] C. Decker, H. Le Xuan, and T. Nguyen Thi Viet, "Photocrosslinking of functionalized rubber. III. Polymerization of multifunctional monomers in epoxidized liquid natural rubber," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 34, no. 9, pp. 1771–1781, 1996, doi: 10.1002/(SICI)1099-0518(19960715)34:9<1771::AID-POLA15>3.0.CO;2-3.
- [170] D. E. Karalekas and A. Agelopoulos, "On the use of stereolithography built photoelastic models for stress analysis investigations," *Materials & Design*, vol. 27, no. 2, pp. 100–106, Jan. 2006, doi: 10.1016/j.matdes.2004.09.028.
- [171] J. D. Curtis, S. D. Hanna, E. A. Patterson, and M. Taroni, "On the use of stereolithography for the manufacture of photoelastic models," p. 15, 2003.
- [172] B. Steinmann and A. Schulthess, "Liquid, radiation-curable composition, especially for stereolithography," US005972563A, 1999
- [173] B. Steinmann, J. Wolf, A. Schulthess, and M. Hunziker, "Photosensitive compositions," US005476748A, 1995
- [174] T. H. Pang, A. P. Melisaris, W. Renyi, and J. W. Fong, "Liquid radiation-curable composition especially for producing cured articles by stereolithography having high heat deflection temperatures," US006100007A, 2000
- [175] W. Renyi and T. H. Pang, "Liquid, radiation-curable composition, especially for producing flexible cured articles by stereolithography," US 2002/0177073 A1, 2002
- [176] C. M. Roland, "Interpenetrating Polymer Networks (IPN): Structure and Mechanical Behavior," in *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Müllen, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 2013, pp. 1–9. doi: 10.1007/978-3-642-36199-9_91-1.
- [177] R. ; A. Adhikari H. ;. Alghamdi, M. N. ;. et al., *Micro and Nano- structured Interpenetrating Polymer Networks: From Design to Applications*. John Wiley & Sons, 2016, p. 425.
- [178] T. Watanabe, A. Matsumura, Y. Haruta, and T. Ukachi, "Photo-curable resin composition and process for preparing resin-based mold," US5932625A, Aug. 03, 1999 Accessed: Mar. 21, 2021. [Online]. Available: <https://patents.google.com/patent/US5932625A/en>
- [179] Y. K. Jung, K. Kuk, and O. H. Beak, "Ink compositions for 3d printing, 3d printer and method for controlling of the same," WO2016108519A1, Jul. 07, 2016 Accessed: Mar. 21, 2021. [Online]. Available: <https://patents.google.com/patent/WO2016108519A1/en>
- [180] J. V. Crivello, "Radical-promoted visible light photoinitiated cationic polymerization of epoxides," *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 46, no. 5, pp. 474–483, 2009, doi: 10.1080/10601320902797707.
- [181] M. Faustini, L. Nicole, E. Ruiz-Hitzky, and C. Sanchez, "History of Organic–Inorganic Hybrid Materials: Prehistory, Art, Science, and Advanced Applications," *Advanced Functional Materials*, vol. 28, no. 27, pp. 1–30, 2018, doi: 10.1002/adfm.201704158.
- [182] C. Brinker and G. Scherer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing," *Advanced Materials*, vol. 3, no. 10, pp. 912–912, 1990, doi: 10.1186/1471-2105-8-444.

- [183] D. M. Pickup, R. J. Newport, and J. C. Knowles, "Sol-gel phosphate-based glass for drug delivery applications," *Journal of Biomaterials Applications*, vol. 26, no. 5, pp. 613–622, 2012, doi: 10.1177/0885328210380761.
- [184] G. J. Owens *et al.*, "Sol-gel based materials for biomedical applications," *Progress in Materials Science*, vol. 77, pp. 1–79, 2016, doi: 10.1016/j.pmatsci.2015.12.001.
- [185] F. Foroutan, "Sol-Gel Synthesis of Phosphate-Based Glasses for Biomedical Applications," 2015.
- [186] M. Dressler *et al.*, "Sol-gel preparation of calcium titanium phosphate: Viscosity, thermal properties and solubility," *Journal of Sol-Gel Science and Technology*, vol. 62, no. 3, pp. 273–280, 2012, doi: 10.1007/s10971-011-2653-y.
- [187] V. Farano *et al.*, "Dissolution behaviour of a novel sol–gel derived phosphate glass," *Dental Materials*, vol. 33, no. October, pp. e29–e30, 2017, doi: 10.1016/j.dental.2017.08.058.
- [188] F. Foroutan *et al.*, "Novel sol–gel preparation of (P2O5)0.4–(CaO)0.25–(Na2O)X–(TiO2)(0.35–X)bioresorbable glasses (X = 0.05, 0.1, and 0.15)," *Journal of Sol-Gel Science and Technology*, vol. 73, no. 2, pp. 434–442, 2014, doi: 10.1007/s10971-014-3555-6.
- [189] D. Carta, D. M. Pickup, J. C. Knowles, M. E. Smith, and R. J. Newport, "Sol–gel synthesis of the P2O5–CaO–Na2O–SiO2 system as a novel bioresorbable glass," *Journal of Materials Chemistry*, vol. 15, no. 21, p. 2134, 2005, doi: 10.1039/b414885a.
- [190] P. Q. Franco, C. F. C. João, J. C. Silva, and J. P. Borges, "Electrospun hydroxyapatite fibers from a simple sol-gel system," *Materials Letters*, vol. 67, no. 1, pp. 233–236, 2012, doi: 10.1016/j.matlet.2011.09.090.
- [191] K. Vojisavljević, P. Chevreux, J. Jouin, and B. Malič, "Characterization of the alkoxide-based sol-gel derived La9.33Si6O26 powder and ceramic.," *Acta chimica Slovenica*, vol. 61, no. 3, pp. 530–41, 2014, doi: 10.1016/S1002-0721(10)60326-2.
- [192] O. F. Göbel, M. Nedelcu, and U. Steiner, "Soft lithography of ceramic patterns," *Advanced Functional Materials*, vol. 17, no. 7, pp. 1131–1136, 2007, doi: 10.1002/adfm.200600783.
- [193] S. J. Kwon, J. H. Park, and J. G. Park, "Selective growth of ZnO nanorods by patterning of sol-gel-derived thin film," *Journal of Electroceramics*, vol. 17, no. 2–4, pp. 455–459, 2006, doi: 10.1007/s10832-006-5412-7.
- [194] A. Ershad-Langroudi, H. Abdollahi, and A. Rahimi, "Mechanical properties of sol–gel prepared nanocomposite coatings in the presence of titania and alumina-derived nanoparticles," *Plastics, Rubber and Composites*, vol. 46, no. 1, pp. 25–34, 2017, doi: 10.1080/14658011.2016.1245821.
- [195] S. Saeed, R. M. Al Soubaihi, L. S. White, M. F. Bertino, and K. M. Saoud, "Rapid fabrication of cross-linked silica aerogel by laser induced gelation," *Microporous and Mesoporous Materials*, vol. 221, pp. 245–252, 2016, doi: 10.1016/j.micromeso.2015.09.012.
- [196] S. Messaddeq and S. Pulcinelli, "Microstructure and corrosion resistance of inorganic–organic (ZrO 2–PMMA) hybrid coating on stainless steel," *Journal of non-crystalline solids*, vol. 247, no. 1–3, pp. 164–170, 1999, doi: 10.1016/S0022-3093(99)00058-7.
- [197] S. A. Omar, J. Ballarre, and S. M. Ceré, "Electrochimica Acta Protection and functionalization of AISI 316 L stainless steel for orthopedic implants : hybrid coating and sol gel glasses by spray to promote bioactivity," *Electrochimica Acta*, vol. 203, pp. 309–315, 2016, doi: 10.1016/j.electacta.2016.01.051.
- [198] V. G. Kessler, *Handbook of Sol-Gel Science and Technology*. 2017. doi: 10.1007/978-3-319-19454-7.
- [199] A. A. Issa and A. S. Luyt, "Kinetics of Alkoxysilanes and Organoalkoxysilanes Polymerization: A Review," *Polymers*, vol. 11, no. 3, Art. no. 3, Mar. 2019, doi: 10.3390/polym11030537.

- [200] V. G. Kessler, *Handbook of Sol-Gel Science and Technology*. 2017. doi: 10.1007/978-3-319-19454-7.
- [201] P. Albert, G. Lohden, C. Gall, and B. Borup, "Ormocers, method for their production and their use," 2009023471, 2001 doi: 10.1037/t24245-000.
- [202] C. Sanchez, P. Belleville, M. Popall, and L. Nicole, "Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market," *Chemical Society Reviews*, vol. 40, no. 2, pp. 696–696, 2011, doi: 10.1039/c0cs00136h.
- [203] J. Wang, T. J. Shi, and X. C. Jiang, "Synthesis and characterization of core-shell $\text{ZrO}_2/\text{PAAEM/PS}$ nanoparticles," *Nanoscale Research Letters*, vol. 4, no. 3, pp. 240–246, 2009, doi: 10.1007/s11671-008-9232-3.
- [204] U. Posset, F. Institut, and D. W., "Radiation curing of hybrid polymer coatings," vol. 89, no. March, pp. 41–48, 2006.
- [205] Y. Mancelog, "The novel use of organo alkoxy silane for the synthesis of organic – inorganic hybrid coatings," vol. 352, pp. 2143–2151, 2006, doi: 10.1016/j.jnoncrysol.2006.02.029.
- [206] C. Belon, M. Schmitt, S. Bistac, C. Croutxé-barghorn, and A. Chemtob, "Applied Surface Science Friction and wear properties of hybrid sol – gel nanocomposite coatings against steel : Influence of their intrinsic properties," *Applied Surface Science*, vol. 257, no. 15, pp. 6618–6625, 2011, doi: 10.1016/j.apsusc.2011.02.088.
- [207] M. Sangermano, E. Amerio, A. Priola, A. Di Gianni, and B. Voit, "Preparation and Characterization of Acrylic Resin / Titania Hybrid Nanocomposite Coatings by Photopolymerization and Sol – Gel Process," 2006, doi: 10.1002/app.24707.
- [208] R. Nagarjuna, S. Challagulla, P. Sahu, S. Roy, and R. Ganesan, "Polymerizable sol–gel synthesis of nano-crystalline WO_3 and its photocatalytic Cr(VI) reduction under visible light," *Advanced Powder Technology*, vol. 28, no. 12, pp. 3265–3273, 2017, doi: 10.1016/j.appt.2017.09.030.
- [209] S. Challagulla, R. Nagarjuna, S. Roy, and R. Ganesan, "Scalable Free-Radical Polymerization Based Sol-Gel Synthesis of SrTiO_3 and its Photocatalytic Activity," *ChemistrySelect*, vol. 2, no. 17, pp. 4836–4842, 2017, doi: 10.1002/slct.201700570.
- [210] D. P. Dworak and M. D. Soucek, "Protective space coatings : a ceramer approach for nanoscale materials," vol. 47, pp. 448–457, 2003, doi: 10.1016/S0300-9440(03)00135-8.
- [211] P. Coudray, P. Etienne, and Y. Moreau, "Integrated optics based on organo-mineral materials," vol. 3, no. 2000, pp. 331–337, 2001.
- [212] R. Ganesan *et al.*, "Direct nanoimprinting of metal oxides by in situ thermal co-polymerization of their methacrylates," *Journal of Materials Chemistry*, vol. 21, no. 12, p. 4484, 2011, doi: 10.1039/c0jm04105j.
- [213] S. S. Dinachali, M. S. M. Saifullah, R. Ganesan, E. S. Thian, and C. He, "A universal scheme for patterning of oxides via thermal nanoimprint lithography," *Advanced Functional Materials*, vol. 23, no. 17, pp. 2201–2211, 2013, doi: 10.1002/adfm.201202577.
- [214] R. Ganesan, J. Dumond, M. S. M. Saifullah, S. H. Lim, H. Hussain, and H. Y. Low, "Direct patterning of TiO_2 using step-and-flash imprint lithography," *ACS Nano*, vol. 6, no. 2, pp. 1494–1502, 2012, doi: 10.1021/nn204405k.
- [215] R. Ganesan *et al.*, "Direct nanoimprint lithography of Al_2O_3 using a chelated monomer-based precursor," *Nanotechnology*, vol. 23, no. 31, 2012, doi: 10.1088/0957-4484/23/31/315304.
- [216] R. Nagarjuna, M. S. M. Saifullah, and R. Ganesan, "Oxygen insensitive thiol–ene photo-click chemistry for direct imprint lithography of oxides," *RSC Advances*, vol. 8, no. 21, pp. 11403–11411, 2018, doi: 10.1039/C8RA01688G.

- [217] S. H. Mir, L. A. Nagahara, T. Thundat, P. Mokarian-Tabari, H. Furukawa, and A. Khosla, "Review—Organic-Inorganic Hybrid Functional Materials: An Integrated Platform for Applied Technologies," *Journal of The Electrochemical Society*, vol. 165, no. 8, pp. B3137–B3156, 2018, doi: 10.1149/2.0191808jes.
- [218] M. Faustini, D. Grosso, C. Boissière, R. Backov, and C. Sanchez, "'integrative sol-gel chemistry': A nanofoundry for materials science," *Journal of Sol-Gel Science and Technology*, vol. 70, no. 2, pp. 216–226, 2014, doi: 10.1007/s10971-014-3321-9.
- [219] L. Nicole, C. Laberty-Robert, L. Rozes, and C. Sanchez, "Hybrid materials science: A promised land for the integrative design of multifunctional materials," *Nanoscale*, vol. 6, no. 12, pp. 6267–6292, 2014, doi: 10.1039/c4nr01788a.
- [220] L. Nicole, L. Rozes, and C. Sanchez, "Integrative approaches to hybrid multifunctional materials: from multidisciplinary research to applied technologies.," *Advanced materials (Deerfield Beach, Fla.)*, vol. 22, no. 29, pp. 3208–3214, 2010, doi: 10.1002/adma.201000231.
- [221] A. Chiappone *et al.*, "3D Printed PEG-Based Hybrid Nanocomposites Obtained by Sol–Gel Technique," *ACS Applied Materials & Interfaces*, vol. 8, no. 8, pp. 5627–5633, 2016, doi: 10.1021/acsami.5b12578.
- [222] P. Judeinstein and C. Sanchez, "Hybrid organic-inorganic materials : a land of multidisciplinary Chemistry : Synthesis of Hybrid Materials," vol. 6, no. 4, pp. 511–525, 1996.
- [223] R. Lichtenberger and U. Schubert, "Chemical modification of aluminium alkoxides for sol-gel processing," *Journal of Materials Chemistry*, vol. 20, no. 42, pp. 9287–9296, 2010, doi: 10.1039/c0jm00993h.
- [224] F. Ribot and C. Sanchez, "Comments on Inorganic Chemistry : A Journal of Critical Discussion of the Current Literature Organically Functionalized Metallic Oxo-Clusters : Structurally Well-Defined Nanobuilding Blocks for the Design of Hybrid Organic- Inorganic Materials," no. January 2014, pp. 37–41, 1999, doi: 10.1080/02603599908021449.
- [225] C. Sanchez, K. J. Shea, and S. Kitagawa, "Hybrid materials themed issue," *Chemical Society reviews*, vol. 40, no. 2, pp. 473–497, 2011, doi: 10.1039/c0cs00076k.
- [226] K. Velez, J. F. Quinson, and B. Fenet, "Modification study of aluminum sec-butoxide by acrylic acid," *Journal of Sol-Gel Science and Technology*, vol. 16, no. 3, pp. 201–208, 1999, doi: 10.1023/A:1008767218134.
- [227] J. Méndez-Vivar, P. Bosch, V. H. Lara, and R. Mendoza-Serna, "The role of 2-(methacryloyloxy) ethyl acetoacetate in the polymerization of hybrid multicomponent (Si, Ti, Zr) sols of hybrid multicomponent (Si, Ti, Zr) sols," *Journal of Sol-Gel Science and Technology*, vol. 25, no. 3, pp. 249–254, 2002, doi: 10.1023/A:1020216229397.
- [228] R. Lichtenberger, M. Puchberger, S. O. Baumann, and U. Schubert, "Modification of aluminum alkoxides with β -ketoesters: New insights into formation, structure and stability," *Journal of Sol-Gel Science and Technology*, vol. 50, no. 2, pp. 130–140, 2009, doi: 10.1007/s10971-008-1890-1.
- [229] Y. Gotoh, Y. Ohkoshi, and M. Nagura, "Preparation and Viscoelastic Behavior of (Meth)acrylate Ionomers Crosslinked by Titanium(IV), Zirconium(IV) and Niobium(V) Ions," *Polymer Journal*, vol. 36, no. 3, pp. 255–260, 2004, doi: 10.1295/polymj.36.255.
- [230] S. H. Lim, M. S. M. Saifullah, H. Hussain, W. W. Loh, and H. Y. Low, "Direct imprinting of high resolution TiO₂ nanostructures," *Nanotechnology*, vol. 21, no. 28, 2010, doi: 10.1088/0957-4484/21/28/285303.
- [231] P. Stoch, P. Goj, A. Wajda, and A. Stoch, "Alternative insight into aluminium-phosphate glass network from ab initio molecular dynamics simulations," *Ceramics International*, vol. 47, no. 2, pp. 1891–1902, Jan. 2021, doi: 10.1016/j.ceramint.2020.09.018.

- [232] Y. Li, H.-Y. Li, K.-C. Chang, H.-M. Lin, and C.-M. Wang, "Recent developments in organic–inorganic hybrid metal phosphates and phosphites," *Dalton Trans.*, vol. 50, no. 29, pp. 10014–10019, 2021, doi: 10.1039/D1DT01016F.
- [233] D. Carta, D. M. Pickup, J. C. Knowles, M. E. Smith, and R. J. Newport, "Sol–gel synthesis of the P2O5–CaO–Na2O–SiO2 system as a novel bioresorbable glass," *Journal of Materials Chemistry*, vol. 15, no. 21, pp. 2134–2134, 2005, doi: 10.1039/b414885a.
- [234] P. H. Mutin and G. Guerrero, "Hybrid materials from organophosphorus coupling molecules," *Journal of Materials Chemistry*, vol. 15, pp. 3761–3768, 2005, doi: 10.1039/b505422b.
- [235] P. H. Mutin and A. Vioux, "Nonhydrolytic Processing of Oxide-Based Materials: Simple Routes to Control Homogeneity, Morphology, and Nanostructure," *Chemistry of Materials*, vol. 21, no. 4, pp. 582–596, Feb. 2009, doi: 10.1021/cm802348c.
- [236] S. S. Dinachali, M. S. M. Saifullah, R. Ganesan, E. S. Thian, and C. He, "A Universal Scheme for Patterning of Oxides via Thermal Nanoimprint Lithography," *Advanced Functional Materials*, vol. 23, no. 17, pp. 2201–2211, May 2013, doi: 10.1002/adfm.201202577.
- [237] M. Guglielmi and G. Carturan, "Precursors for sol-gel preparations," *Journal of Non-Crystalline Solids*, vol. 100, no. 1–3, pp. 16–30, 1988, doi: 10.1016/0022-3093(88)90004-X.
- [238] K. Velez, J. F. Quinson, and B. Fenet, "Modification study of aluminum sec-butoxide by acrylic acid," *Journal of Sol-Gel Science and Technology*, vol. 16, no. 3, pp. 201–208, 1999, doi: 10.1023/A:1008767218134.
- [239] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, and C. Chau, "Primary hydrolysis products of methacrylate-modified titanium and zirconium alkoxides," *Chem. Mater.*, vol. 4, no. 2, pp. 291–295, Mar. 1992, doi: 10.1021/cm00020a014.