POLITECNICODI TORINO

Master in Nanotechnologies for ICTs

Master Thesis

Photocurable 3D-printable systems with controlled

porosity towards filtering applications



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At first people refuse to believe that a strange new thing can be done, then they begin to hope it can be done, then they see it can be done then it is done and all the world wonders why it was not done centuries ago.

Frances Hodgson Burnett, The Secret Garden

Abstract

The continuous evolution in the field of 3D-printing is leading to the search for new materials with specific characteristics. In this thesis work new materials with controlled porosity will be developed and processed by means of Digital Light Processing (DLP) 3D-printing system. The formulations are based on photocurable emulsion of 1,6-Hexanediol diacrylate, while porous structures are fabricated taking advantage of presence of PLURONIC F-127 surfactant. This ingredient enables the formation of stable micelles that are necessary to create controlled porosity. The formulations contain as well photoinitiator in order to enable polymerization when exposed to UV radiation and UV absorbers and radical scavengers to properly control the extent of reaction in the 3D printer. The porosity of the structures is controlled by changing the water/surfactant ratio, which in turns affects the printing parameters and mechanical properties of the fabricated components. This is evaluated by preliminary tests such as photoreology and materials characterization on the 3D-printed objects. Successful 3D printing of porous structures was achieved with excellent CAD fidelity; the morphology is evaluated using scanning electron microscopy. Furthermore, different shapes were printed to test possible applications in different research fields, such as CO₂ trapping and quality air filtering, which can take advantage of the large available surface area.

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1. Purpose of the thesis

The aim of the thesis is to produce objects with complex structure and with enhanced surface-area-to-volume ratio. The last decade has seen a lot of researches into the synthesis of new microporous materials that have a greater surface-area-to-volume ratio. The surface-area-to-volume ratio is the amount of surface area per unit volume of an object. In chemical reactions involving a solid material, the surface-area-to-volume ratio is a crucial factor for the reactivity of the chemical reaction[1]. A porous material reacts much faster than a compact material due to the presence of greater exposed area able to react. A high surface-area-to-volume ratio provides a strong "driving force" to speed up thermodynamic processes that minimize the thermodynamic free energy. Researchers in recent years deepened this field driven by the numerous applications that these materials may encompass such as molecular separations[2], gas storage[3], drug delivery[4], sensing[5] and catalysis[6]. In particular, porous polymeric materials do not have a welldefined porous matrix and can have a wide range of application tailored to the customer. In this thesis such materials are used to fabricates objects with complex structures, to combine the intrinsic porosity of structures with geometries that improve performance in specific applications. This is made possible thanks to the use of Additive Manufacturing, which allows the creation of complex geometric structures, made using CAD software. Specifically, we will focus our attention on the Digital Light Processing (DLP) method, printing slurry of polymeric substances with intrinsic porosity. The aim of the thesis work is to print 3D structures with porosity and analyze the morphology, chemical and mechanical properties by varying the concentrations of the mixtures and the printing features.

Gathering two levels of complexity, at the macro and at the microscale, can open interesting perspective in numerous application such as catalytic chemistry, energy devices, sensors, and filters.

1.1 The importance of increasing the surface area

In the last few decades, the trend of creating smaller and smaller structures is spreading across the manufacturing and electronics industries. In the field of electronics, the need to have more and more computing power leads us to the need to reduce the dissipated power of each device. This can be done by using smaller transistors, made up of single atoms, to reduce power consumption. As in electronics the density of power can be enhanced miniaturizing the objects, in many application fields the functionality of a material can be increased by increasing the surface-area-to-volume ratio. This can be achieved synthesizing materials with micro/nano-structured surfaces.

The understanding of the effect of surface (nano)structuration on the properties of materials is a point of increasing importance. This knowledge merged with the synthesis of a specially designed materials can bring to the production of object with peculiar properties suitable for different applications.

Currently, there are six classes of materials that are acknowledge for having a high surface area and porosity [7]: porous carbon, porous inorganic materials, crystalline metal organic frameworks (MOFs), crystalline covalent organic frameworks (COFs), and amorphous microporous organic polymers [8].

Porous carbons have been used for years and are now materials with a wide range of applications and of crucial importance for industries. The porosity of these microstructures consists of uniform nanometric pores and are particularly relevant for the adsorption of substances from gases or liquids. Microporous inorganic materials comprise crystalline silicas or zeolite, in which the porous structure is well-defined by a periodic crystalline framework. The use of these materials is mainly related to filtration and sieving, due to a well-defined pore structure. The biggest challenge was to create porous structures with discrete pores with organic polymeric materials. This barrier has been broken down through reticular chemistry, the chemistry of linking molecular building blocks by strong bonds to make crystalline open frameworks, with which porous materials can be synthesized using topologically designed building blocks. There are two families of porous materials synthesized through reticular chemistry: the first family is metal-organic frameworks (MOFs), which consist of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional network structures⁵; the second is covalent organic frameworks (COFs), constructed by pure organic building blocks to form crystalline porous polymers via reversible covalent bonds with predictable control over composition, topology, and porosity [9]. The strength of MOFs and COFs consists in having an ordered and regular porous surface structure. However, often the synthesis of such surfaces is very complex, showing additionally low chemical stability.

Instead of having a well-defined pore size distribution, amorphous microporous materials formed by sol-gel processes have several advantages for applications in membranes, sensor and catalysis [10] due to the fact that a non-uniform distribution of pores size increase the filtering performance.

The most used technique to evaluate the surface area of a microporous material is the Brunauer-Emmett-Teller (BET) method, exploiting the adsorption of a gas on a solid surface. This method is not very effective for the study of micropores, but it still provides a significant comparison between microporous materials. The first surface area measurement dates to 1999, made by Yaghi and co-workers [11], on a MOF material with a measured area of 692 m²/g. From that moment there was an explosion in the study of



Figure 1 - Plot of SA_{BET} versus publication year of materials with high surface area - J. R. Holst and A. I. Cooper, "Ultrahigh surface area in porous solids"

materials with ultra-high surface area, as it is possible to see in (Figure 1). Metal-organic frameworks made up most of the discovered materials with high BET surface area. A milestone material is MOF-177, first discovered in 2004 with a BET surface area of 4508 m^2/g , further improved to 4746 m^2/g in 2006 [12]. The first crystalline covalent-organic framework was discovered from Yaghi and co-workers in 2005 [13], a material made by light element (C, H, O, B, Si), also the first examples of two-dimensional layered structures with 1-dimensional pore channels [8]. At the beginning COFs surface area is less than the MOFs one, but a substantial increase was observed in 2007, with the first three-dimensional structures, reaching a BET surface are of $3472 m^2/g$ [14]. The turning point was the discovery of porous organic polymers, many of which are amorphous in nature. To the detriment of a well-defined porous structure, their advantage is to introduce any chemical functionality much more easily. The great discovery was made by Ben *et al.* [15], with a robust polyphenylene network, called PAF-1 (Figure 2), with a remarkable surface area of 5640 m^2/g . This porous organic polymer is the proof that is not necessary



Figure 2 - Examples of high surface area materials - J. R. Holst and A. I. Cooper, "Ultrahigh surface area in porous solids"

to have a long-range order for obtaining an ultra-high surface area. The evolution of porous polymers is the solution-processable "polymers of intrinsic micro-porosity" (PIMs), with in general less porosity, but better suited for commercial applications.

In recent years, microporous polymers have attracted more and more the attention of researchers due to their high chemical stability, thanks to covalent C-C, C-H and C-N bonds, in spite of a long-range order [16]. Polymers also have the potential of exploiting a particular design to enhance surface area and well-defined porosity [15]. Porous polymers have easy processability, they can be fabricated in monolithic form [17] or in thin films [18], giving a lot of advantages in practical applications. Polymers can be dissolved in solvent, improving the quantity of realization techniques. One of the most important advantage is that porous polymers are able to incorporate multiple chemical functionalities [19] increasing significatively the number of applications of these structures. Polyurethanes are examples of polymeric materials that can provide an adequate porous structure. In the biomedical field, polyurethanes are used in the production of implantable devices in contact with blood and soft tissues. The advantage of polyurethanes compared to other polymeric materials lies in the versatility of this type of polymers: through an appropriate selection of reagents and their stoichiometric ratios, it is possible to obtain extremely different materials, with different mechanical properties, biocompatibility, and biodegradability[20]. In the synthesis phase it is therefore possible to design ad hoc materials for the specific application required.

Researchers in recent years have been deepening this field driven by the numerous applications that these materials have such as energy storage and separations technologies, thermal barrier materials for use in high-temperature engines, biochemical and pharmaceutical separation molecular separations, and catalysis.

The hydrogen economy is the use of hydrogen as a fuel for heat, hydrogen vehicles, seasonal energy storage, and long-distance transport of energy. In order to limit global warming, hydrogen can also be created from water, and its combustion only releases water vapor to the atmosphere. Given the current worldwide interest in reducing emission form energy production it is not surprising that the storage of gases that can be used for energy applications is attracting a great deal of attention.

The use of porous materials to store energy is increasingly developing, while the use in the medical field is already a reality and very close to commercialization. In this field, works are focused on the use of polymers. In most cases the porosity of the polymers is not well defined, but it is clear from the adsorption capacity of the gases. The main application consists in controlling the release kinetics of the gases, due to the fact that the gases of interest are often toxic in large amount, while they may be ineffective if delivered in too small amounts (e.g. NO and CO) [3].

Separation, storage, and removal of relevant gases would contribute to green energy utilization and environment protection. Porous materials are also known in these applications. Nitrogen oxides or Sulphur dioxide are deleterious for the environment, contributing to the formation of haze, acid rain, and anthropogenic climate change. High porosity, variable pore size, and high concentrations of active adsorption sites make porous materials an appealing class for these applications [21].

As we have seen given the numerous applications, microporous materials are crucial materials for technology and development in future centuries. Scientists are now adapting the chemical and physical characteristics of these materials to the needs of humanity, creating ad-hoc structures for every need. In fact, thanks to additive manufacturing, it is possible to print objects with complex geometries made-up by these materials, combining to increase the field of application previously limited by the physical structure of the materials.

2. Additive Manufacturing

As Theodore Levitt said, "People don't want a quarter inch drill, they want a quarter inch hole".

Additive Manufacturing is the construction of a three-dimensional object from a CAD model with measures and characteristics that the operator requires. It is a production technique that allows fabricating objects with extremely complex shapes without material waste and without using moulds [22], making it a viable alternative to subtractive manufacturing techniques.

2.1 History of Additive Manufacturing

The first equipment and materials for additive manufacturing were developed in the 1980s. Hideo Kodama invented two additive methods for fabricating three-dimensional plastic models with photo-hardening thermoset polymer, where the UV exposure was controlled by a mask pattern or a scanning fibre transmitter. To have the first 3D-printer it took until 1984, when Chuck Hull filed his own patent for a stereolithography fabrication system, in which layers are added by curing photopolymers with UV light lasers. Hull defined the process as a "system for generating three-dimensional objects by creating a cross-sectional pattern of the object to be formed" [22].

Stereolithography is one of the first known process, followed by powder bed fusion, fused deposition modelling (FDM) and inkjet printing. Over the years, AM (Additive Manufacturing) has been applied to various sectors, such as biomedical, aerospace, mechanical, automotive and construction sectors. Regarding the latter, development is

very slow, but slowly it is gaining ground to favor less waste and freedom of designing spaces. The reason why this technology is becoming more and more widespread is the reduction of costs of 3D printers, which makes it more accessible even for schools, laboratories or even for personal use. Why preferring 3D printing to mass production? 3D-printing allows you to create small quantities of products at very low costs, differently than mass production; moreover, it does not have to rely on different production lines to obtain the finished product. Mass production needs a team that works on the product continuously, as opposed to 3D-printing where you just have to upload a file to a computer and that's it. As we can see from (Figure 3), 3D-printing has a narrower, but more particular, market segment.

Characteristic	Mass Customization	3-D Printing
Manufacturing Technology	Based on pre-assembled modular parts in different combinations or delayed differentiation.	Automated manufacturing based on CAD software and additive manufacturing.
Supply Chain Integration Requirements	Need for highly-integrated supply-chain management to ensure right goods at right times from multiple supplies.	Uses readily available supplies available from multiple vendors.
Economic Benefits	Ability to produce custom products at relatively low prices. Low inventory risk. Improved working capital management.	Ability to produce custom products at relatively low prices. Low inventory risk. Improved working capital management.
Range of Products	Computers; watches; windows; shoes; jeans.	Prototypes; mockups; replacement parts; dental crowns; artificial limbs.

Figure 3 - A comparison of mass customization and 3D-Printing - Barry Berman, 3-D printing: The new industrial revolution

The evolution of 3D-printing can be summarized through three citations: The first phase is "It's cheap to do this stuff... It costs the same to produce two different variants as two identical ones. The economies-of-scale rationale of serial production does not apply" [23]: the main use was aimed at prototyping, thanks to an easy duplication of products, low price, and the possibility of quickly modifying the prototype to test the various versions. The second phase can be synthetized with "With 3D-printers onsite, prototypes can be produced in just a few hours": 3D-printing was used mainly in test marketing, different size, different colours and styles- could be more easily produced and market tested. The last phase is the future: "My hope is that people, instead of going to the store, will go online and download what they need and print it out" [23] This is particularly useful in the biomedical field, where customized patient-specific products are typically required like dental crowns or artificial limbs.

2.2 Main methods

The different types of Additive Manufacturing have developed over time following the needs of consumers, such the need to print a tiny high-precision structure, print a large surface reducing possible printing defects and improving the chemical-mechanical capabilities of the final product. The most popular 3D-Printing methods use polymer filaments (FDM) [24], or additive manufacturing of powders by selective laser sintering (SLS) and selective laser melting (SLM) [25], electron beam melting (EBM) [26] or liquid binding in three-dimensional printing (3DP), as well as inkjet printing, contour crafting, stereolithography, direct energy deposition (DED) [27] and laminated object manufacturing (LOM) [28]. These are the best-known techniques and can be applied to different types of media by varying only some printing specifications. There are also more recent and specific methods for certain applications, such as two-photon polymerization (TPP), used to create ultraprecise 3D structures for nano-photonics, microfluidics, or biomedical implants; projection micro-stereolithography (PµSL) [29] is quite like the conventional SLA method, the difference is that PuSL the UV light polymerize the entire cross-section in a single exposure; the electrohydrodynamic printing (EHDP) involves electric-field viscous fluid jet with functional inks. To choose the best method to print a certain object, must be take into account the material with which the object has to be printed.

2.2.1 Metals and alloys

In recent years, companies selling Additive Manufacturing products increased visibly, of which half use metal additive manufacturing. Metal AM provides an ample freedom for creating complex structures and solutions to structural, protective engineering and insulation problems at the same time.

The main methods of Metal AM consist in melting powder or wire with a power source such as laser, arc discharge or electron beam. The most used techniques are powder bed fusion and direct energy deposition. Powder bed fusion (PBF) consist in thin layers of powders, produced ad-hoc respecting strict requirements in terms of particle size, size distribution and mechanical strength, fused in each layer together with a laser beam or a binder, depends on the powders melting temperature. Selective laser sintering can be used for a large variety of materials, such as polymers, metals and alloys, the drawback is that the powders are not completely melted. Selective laser melting instead, can be used just for steel or aluminum, but provides a better powders fusion. The biggest difference between processes in the PBF methods is the use of a liquid binder. The chemical features, size and shape of the binder play a crucial role in the printing process, providing a larger porosity of the product with respect to the ones printed without the binder.



Figure 4 - Laser Powder-Bed Fusion 3D Printing Process - Kuelper, Kristofer. (2019). DYNAMIC MECHANICAL RESPONSE OF ADDITIVELY MANUFACTURED 316L AND AlSi10Mg.

The main advantages of powder bed fusion are fine resolution, high quality of printing and the absence of difficulties in removing the sample from the supporting material, due to the fact that the powder is the support itself. The biggest drawback, as said before, is the porosity obtained during the printing process when a binder is used.

Direct energy deposition (DED) has been used for high-performance super-alloys manufacturing. DED used an energy source focused on the substrate to melt the material, that is than deposited on the melted substrate and solidified after the movement of the beam. The main difference with the powder bed fusion is that in DED there is no vat with powder, the material is melted before the deposition. About the precision, DED has a lower accuracy with respect to SLS or SLM, in fact it is used for filling cracks, for creating low complexity products. The advantages consist in low manufacturing time and cost, and excellent mechanical properties, due to the fact that there is a high composition control.



Figure 5 -In direct energy deposition (DED), a metal feedstock is introduced to an energy source in the form of a wire (A) or as a powder (B) - Michael Molitch Hou, 1 - Overview of additive manufacturing process, Editor(s): Jing Zhang, Yeon Gil Jung, Additive Manufacturing, Butterworth-Heinemann, 2018, Pages 1-38

2.2.2 Ceramics

Despite the accuracy of the printed parts and a limited selection of materials, also ceramics can be treated through additive manufacturing. The main feature that characterize ceramics is the possibility to control and tune the porosity inside the printed system. In this way, ceramic additive manufacturing improves the development of lightweight material tailored for different applications. Porosity is a way to change the surface area of the system and the mechanical properties. Li et al. [29] developed a porous alumina ceramic with the addition of CaSO₄ and dextrin, which showed a very high flexural strength.

The most used method to ceramic 3D-printing are inkjet, powder bed fusion and stereolithography. SLS is also a used method, but the thermal shock created between the fusion and the cooling phase can lead to crack formation in ceramic parts. Stereolithography is recently used also for ceramic instead of the traditional use for photopolymerization, but the material able to be used are low, in fact materials with a better light scattering properties are preferred to provide a better light curing of the binder.



Figure 6 - Image from U.S. Patent 4575330 introducing the term and the concept of stereolithography.57 Description of components using the numbering scheme from the patent: (21) container, (22) UV curable liquid, (23) working surface, (26) UV light source, (27) UV light spot, (28) computer, (29) movable elevator platform, (30) three-dimensional object, and (30a-c) integrated laminae of the object.

2.2.3 Polymers and composites

Polymers are the materials most used in the 3D-printing industry thanks to their diversity and their capability to adapt itself at different printing methods. Polymers can be used in form of thermoplastic filaments, reactive monomers, powders, or slurry. Various 3Dprinting methods, as said before, are available for fabricating polymers and composites, such as SLS, FDM, inkjet printing, but the most used is stereolithography.

Stereolithography works by collimating a coherent beam of light, usually an UV laser, on a vat containing a photosensitive resin. With the help of a programmed software, the UV laser is used to "draw" the desired structure on the tray, layer by layer. There are two different printing methods, top-down and bottom-up, and consequently two different systems of printer operation. In the first case, the top-down, as the word itself suggests, the laser is focused on the vat containing the photosensitive resin, this is polymerized forming the desired layer. Once the first layer is finished, the build platform is lowered, the vat is refilled with resin, and the process is repeated until the structure is complete.



Figure 7 - An illustration of the multi-material SL process based on top-down projection - Zhou, C., Chen, Y., Yang, Z. and Khoshnevis, B. (2013), "Digital material fabrication using mask-image-projection-based stereolithography", Rapid Prototyping Journal, Vol. 19 No. 3, pp. 153-165

The second method allows to print a structure from the bottom up. This is possible by using a vat with a transparent bottom and aiming the laser beam upwards through the bottom of the vat. It is filled with resin, the build platform lowered until it touches the bottom of the tray and the UV laser writes the lowest layer of the structure. Then the build platform rises, and the cured layer remains attached to the platform. The process is repeated until the construction is finished. This second method shows numerous advantages over the first, it is to be able to build larger structures than the vat dimension that contains the resin, and there is no need for a continuous filling of the vat. Just make sure to have enough resin inside the tray. Generally, in this printing method the structures need supports to remain anchored to the build platform during printing, and these are created by the printing software and subsequently removed at the end of the print.



Figure 8 - An illustration of the multi-material SL process based on bottom-up projection - Zhou, C., Chen, Y., Yang, Z. and Khoshnevis, B. (2013), "Digital material fabrication using mask-image-projection-based stereolithography", Rapid Prototyping Journal, Vol. 19 No. 3, pp. 153-165

One of the main advantages of SLA is the high spatial resolution provided by the spot size of the focused laser beam. With SLA, light exposure is performed sequentially, pointby-point, so the time necessary to produce one slice of the structure therefore depends on the speed with which the laser beam is scanned and on the illuminated area [28].

2.3 Digital Light Processing

The light-based 3D-printing, such as stereolithography (SL) makes light curing the key process of printing. A very promising printing method in this field is Digital Light Processing (DLP) which uses photopolymerization, but unlike the previous methods, the polymerization is not activated point by point, but a projector is placed under the vat and

illuminates the whole layer at the same time. This implies some precautions to be made regarding the materials and resins used in this process, which must be transparent enough to allow the correct absorption of light, without however causing an overexposure of the layer which would lead to errors during printing, such as over-polymerization of the layers, causing an incorrect geometry of the final printed pieces. The most important part of the printer is the digital micro-mirror device (DMD), which consists of a group of small controllable mirrors, to control the optical path of the light and then project it correctly onto the vat containing the resin during the process. The resolution of the print depends on the DMD and the lenses used, and therefore has a very low resolution, generally on the micron scale. Furthermore, as mentioned before, each layer is not scanned point by point but at the same time, greatly reducing the printing time.



Figure 9 - Schematic diagram showing the working principle and related application fields related to DLP based 3D-printing technology - International Journal of Bioprinting (2020) - Volume 6, Issue 1

The materials used in the DLP printing process are photopolymers made up of various elements, such as monomers, oligomers, photoinitiator and other additives like dye, or fillers. Each of them plays a very specific role during printing.

Choosing the monomers, or the oligomers, depends firstly on the functionality that we want in the mixture, then viscosity, reaction kinetic, mechanical, and functional properties

are considered. The fundamental element is the photoinitiator, that is the molecule that absorbs the light radiation and initiates the photopolymerization process, generating new active species and creating new chemical bonds. It determines the efficiency of the polymerization reactions, which influence all of the printing specification, such as resolution and accuracy. The dyes instead are linked to the ability to obtain a higher resolution of the printing process. In fact, the photoinitiator absorbs light, but to have greater control of the penetration of light, it is necessary to have other absorbent materials. Controlling the amount of dye inside the mixture is essential, as in case of excess the light cannot penetrate deeply, causing poor adhesion between the layers or even completely inhibiting photopolymerization, as we will see in the next chapters when we analyze the polymerization kinematics of the mixture by varying the concentrations of the elements present in it.

2.4 Photopolymerization

Polymerization is defined as the generation of long-chain macromolecules, formed by the continuous addition of monomers or oligomers. Specifically, in photopolymerization, the addition is caused by stimuli of energy provided by light. Light curing depends not only on the amount of light that is emitted, but also on its wavelength. The photopolymerization takes place if the wavelength of the light overlaps the wavelength of the photoinitiator present in the mixture, which absorbs the light and transforms it into chemical energy in the form of free radicals or free cations, hence the diversification into the various photopolymerization processes.





A different result is also obtained according to the type of monomer/oligomer used in the process. By using monofunctional monomers, the result than can be obtained is simply a linear chain, however, by using multifunctional monomers or oligomers, i.e. which contain at least two functional groups, photopolymerization shows a more complex behaviour, giving rise to three-dimensional structures, through a process called photocrosslinking. The main components of a photopolymerization process are therefore the monomers, the light crosslinking oligomers and the photoinitiator.

The definition of oligomer is a molecule composed of a limited number of small repeating units (monomers), and in the photopolymerization process it is the material with the highest viscosity and it is the one that most affects the structure of the final product. The greater the amount of oligomer in a formulation, the higher the viscosity and the lower the solubility of the photoinitiator. Viscosity in a 3D-printing process is a fundamental parameter, and furthermore, if the photoinitiator is not well solubilized, the photopolymerization process does not take place correctly. On the other hand, monomers, unlike oligomers, act as solvents in the formulation and decrease its viscosity, affecting the physical and mechanical properties of the product. Monomers also play a fundamental role in printing times, in fact the higher the number of functional groups present in the monomer, the faster the reaction speed of the chains will be, thus decreasing the printing time.

The photoinitiator, as said in the previous section, affects the properties of the final product, in fact, the efficiency and the polymerization rate, influence the mechanical properties of the printed part. It is the key element of the process, the one who initiates the polymerization reaction by absorbing the light intensity and transforming it into chemical energy.

Finally, the dyes, as mentioned in the previous paragraph, help to have greater control over the definition of the print. Together with the photoinitiator, they are absorbent elements, which, when dosed well, manage the absorption of light intensity, avoiding over-polymerization and consequent errors in the final geometry of the product.

Based on the active species generated by the photoinitiator to convert light into chemical energy, we can distinguish two different types of polymerization, radical polymerization, and ionic polymerization, which in turn can be anionic or cationic. In cationic polymerization, the growth of the chain occurs through the electrophilic attack of the macro-cation to the monomer, the anionic mechanism instead is represented by a nucleophilic attack on the monomer by the propagating anion. Free-radical polymerization is a method of polymerization in which a polymer forms by the successive addition of free-radical building blocks. Anionic polymerizations are difficult to carry out and are only used on an industrial scale if the monomer in question does not polymerize by free-radical mechanism or when polymers with regular structure are required. It is often the method of choice for the synthesis of well-defined block copolymers. Free-radical polymerization is the most versatile type of chain-growth polymerization. Because of the non-specific nature of the free radicals towards vinyl monomers, many monomers can be copolymerized. Other advantages in favour of radical polymerization is the lower economic cost and the greater reactivity.

We can divide radical photo-polymerization into three stages: initiation, propagation, and chain transfer (and consequent termination).

The initiation phase in turn consists of two reactions, the first consists in the production of free radicals generated as a result of the dissociation of the photoinitiator due to the effect of light radiation. The radical species generated, highly unstable, tends to react quickly with the monomer present in the mixture, generating the propagating species. The

$In \xrightarrow{k_{d}} In^{\bullet}$ $In^{\bullet} + M \xrightarrow{k_{i}} M_{1}^{\bullet}$	initiation
$\sim M_n^{\bullet} + M \xrightarrow{k_p} \sim M_{n+1}^{\bullet}$	propagation
$\sim M_n^{\bullet} + RH \xrightarrow{k_{tr}} \sim M_nH + R^{\bullet}$	chain transfer
${}^{\sim}M_n^{\bullet} + In^{\bullet} \xrightarrow{k_t^p} dead polymer$	primary termination
$^{M_n^{\bullet}} + ^{M_m^{\bullet}} \xrightarrow{k_t^{b}} \text{dead polymer}$	bimolecular termination
$\sim M_n^{\bullet} \xrightarrow{k_t^m} (\sim M_n^{\bullet})_{trapped}$	monomolecular termination

Figure 11 - Stages of photopolymerization - Ewa Andrzejewska, Chapter 2 - Free Radical Photopolymerization of Multifunctional Monomers

reaction rate of the two processes is defined by the rate constants k_d and k_i , respectively the constant of the dissociation process and that of generating the initiator radical [30]. The overall speed of the first state of the photopolymerization reaction depends on the intensity of the absorbed light (which is not equal to the intensity of the emitted light), and on the quantum yield for initiation, defined with the symbol phi. The correction factor 2 is a consequence of the fact that two radicals are produced per molecule.

The second phase of the process is propagation, which consists in the growth starting from the initiator radical of a chain composed of hundreds of monomeric molecules. Each addition creates a further radical of the same type as the previous one, unlike the size. The propagation speed is defined through a constant k_p, which is generally very high for monomers [30].

The propagation of the polymer chain ends in the third stage of the process, the termination. The radical centres are destroyed or eliminated. Termination can occur

between macroradicals and primary radicals, this occurs when there is a high production of primary radicals due to a high absorbed light intensity or a high concentration of photoinitiator. It can occur through the reaction of two macroradicals, the most frequent termination process in polymerization. The last type of termination is the entrapment: the elimination of radicals occurs during the formulation of the network and at high temperatures.

3. Applications of porous 3Dprinted materials

Porosity, regardless of the type of material used, is one of the main causes for which the mechanical, physical, and chemical characteristics are affected.[31] For example, high porosity can decrease the stiffness of a material in relation to its fully solid counterpart. Increasing porosity also means increasing the surface area available in a material. J. Guo and J.M. Catchmarks found that CNWs show a significant increase in surface area and porosity compared to fibrous cellulose[32]. Bae, Erdonmez, Halloran, and Chiang discovered how joining a porous matrix within aligned channels within a battery significantly improves the cell-discharge rate[33]. Another field of application is that relating to chemical reactions that depend on catalytic reactions and consequently on the available surface. The excellent catalytic performances are attributed to the high porosity and the large number of interfaces[34]. From a biological point of view, porosity in materials has proved to be a crucial component for tissue integration or for the incorporation of cells and growth factors to regenerate damaged tissues or organs[35]. In this sector, meticulous control of the pore size is necessary, small pores promote hypoxic conditions and induce osteochondral formation before osteogenesis, while large pores, that are well-vascularized, lead to direct osteogenesis[36]. This trend results in diminished mechanical properties. A compromise must therefore be found between the two situations, based on the application for which they were created. The applications listed above are only a part of the many positive aspects of porous materials. The important role that porosity within materials is playing has led scientists to investigate

this sector, prompting them to search for new solutions to create ad-hoc structures, tailored to the application that will be implemented. Porous ceramics with different porous morphology and size distribution can be fabricated mainly by three different methods. The first is the use of porogens, a mass of particles, of a specified shape and size, used to make pores in moulded structures used for tissue engineering, dissolved

____ 100 μm



Figure 12 - Optical photographs of porous ceramics fabricated by gelcasting - F.-Z. Zhang et al. / Journal of the European Ceramic Society 26 (2006) 667–671

away after the structure has set. The second is the degradation of the material itself. At a certain temperature the material begins to degrade, and the release of gas contributes to the creation of pores inside the structure. The last one consists in the use of templants, that is material and / or structures that can be removed from the melded piece at a later time, for example through a solvent wash.

These techniques mentioned are those that underlie the porosity creation process, in fact they can be combined with other techniques, such as burning out a polymeric sponge impregnated with a ceramic slurry, solid-state sintering, sol–gel process, replication of polymer foams by impregnation, and gelcasting process[37].

The gelcasting process exploits the foaming of aqueous slurry, the difference lays in the controlling system. In traditional process, the slurry is immediately gelling in a N₂ system.

This does not happen in the new methods, in fact, some bubbles may shrink and disappear, others may coalesce to form larger bubbles. The changes in the foam structure are important because affects the pores distribution, obtained a non-uniform final structure. These types of porous matrix can be used for a wide range of applications, such as filters, membranes, sensors, or catalyst carriers. These methods do not allow full control of processes, such as total porosity, pore size, distribution, and shape.

Zeolites are a family of crystalline aluminosilicate mineral[38] whose structure is composed of ordered micropores, with an average diameter of 2 nm. The size of the pores depends on the structure of the zeolite. These are materials widely used in the porous structures sector thanks to the high gas absorption capacity, caused by the high specific surface area. This feature is exploited for adsorption, separation, and catalysis. New application are discovered in recent years, such as optoelectronics, sensing or drug delivery[39]. Nevertheless, the presence of such micropores impose limitations, such as the diffusion of the reactants. In fact, less than the 10% of active sites participate actively in the catalytic reaction[39]. To overcome to these limitations, many solutions has been developed over the years, like the synthesis of zeolites with extra-large micropores or obtaining zeolite samples with intracrystalline mesopores, generating mesopores during the zeolite crystallization using a template[40].

To introduce precise porosity control, other creation processes have been used, the most used being additive manufacturing and 3D-printing.

3.1 3D-printable porous materials

Using additive manufacturing to fabricate well-defined structures presents new opportunities for engineers to study and design objects with completely different designs.

3D-printing offers the potential to create completely homogeneous structures with predefined CAD arrangements, including position, orientation, and pore size.

There are many 3D printing techniques that allow the creation of porous ceramic parts such as Stereolithography (SLA), Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Fused Deposition Modelling (FDM) and Binder based 3D printing[41]. Stereolithography to create 3D structures uses photocurable slurry, which is solidified by a UV source through the photopolymerization process. SLS and SLM instead use a laser source to sinter and melt the powders respectively. In FDM, the filament can be composed of a mixture of ceramic and binders, and deposited layer by layer through a nozzle. These are the most used techniques, preferred to the others for their simplicity and low cost[42]. However, ceramics are limited to those with high melting temperature, thus resulting in difficulty in fused deposition[43].

SLA is the most flexible of the techniques because it allows to design parts with any shape or size. It uses UV light to initiate a chain reaction on a layer of resin or monomer solution. The monomers are UV-active and instantly convert to polymer chains after activation. After polymerization, a pattern inside the resin is solidified in order to hold the sequent



Figure 13 - Radial design (left) and orthogonal design (right) HA implants for the in vivo evaluation²¹

layer[44]. Ceramic porous structures are designed to promote tissue regeneration, growth, and anchoring of bones in transplants. In the biomedical industry, creating scaffolds for tissue and organ replacement requires advanced knowledge of the scaffold being used. The scaffolds must have an open-pore geometry with a highly porous surface and microstructure that allows cell in-growth and reorganization in vitro and provides the necessary space for neovascularization from surrounding tissues in vivo[45]. The size of the pores must also be controlled. Tissue regeneration depends on the size of the pores, a dimension linked to the type of tissue that must regenerate.

To regenerate adult mammalian skin, pores with a diameter between 20 and 125 μ m are used, between 45 and 150 μ m instead for the regeneration of liver tissues[46]. Chu et al.[47] treated bone regeneration in the lower jaw of Yucatan minipigs using SLA to produce hydroxyapatite scaffolds with two different pore matrix. The results showed that as the porous matrix of the structure changed, the distribution, quantity and function of the tissues that were generated also changed. The main drawbacks of SLA is the use of radicals and photoiniators that may be cytotoxic over a long time period, due to the



3DP™ MODEL

Figure 14 - Craniofacial skeleton obtained through a tomography technology fabricated by Selective Laser Sintering²⁴

entrapment of residual unreacted monomer and photoinitiator[41]. The major advantage is its ability to create a well-defined architecture.

SLS can fabricate complex ceramic structures. This technique is used by Xia et al.[48] to fabricate scaffolds which showed a good biocompatibility and promotion of healing for bone defect. The sintering process does not involve complete melting of the ceramic powder, so the porosity of the original ceramic particles can be maintained[49]. Silva et al.[50] used SLS for prototype fabrication of a craniofacial skeleton from an image obtained through a tomography technology. A dimensional error of 2.10% was observed. The replication achieved a high level of accuracy except for thin bones, small foramina, and acute bone projections.

SLM process need higher power with respect to SLS process. Powder is melted by a laser according to CAD data. The advantages of these techniques is their ability to manufacture high fracture toughness and good mechanical properties for load-bearing application[41]. The dimensions of pores depends on the used ceramic powder.

FDM technique create 3D objects from computer generated models, obtained from magnetic resonance, tomography scans or CAD files. The most common application is the creation of ceramic scaffolds, that can have interconnected channel networks, high



Figure 15 - Micrograph showing three-dimensional pore interconnectivity within FDM-fabricated structure¹⁶
channel size and controllable porosity[51]. A research performed by Tseng et al.[52] demonstrates that to control the structure of a fabricated scaffolds, four criteria have to be considered. These are the width of the road, thickness of slice, angle, and gap raster. In recent years, 3D printing has been developing rapidly, making significant strides in the area of printing resolution, materials used and printing speed. 3D printing offers the possibility of producing green bodies by meticulously controlling their external shapes and internal characteristics, such as the size of the pores, through a CAD software. Evolution does not only include the biomedical sector. The production of porous ceramic structures can be used for catalysis[53], filtration technologies, production of automotive parts, adsorption[54], separation[55], sensors[56], and energy[57]. The intrinsic porosity inside a structure gives to objects properties such as high permeability, high surface area, and good insulating characteristics.

The increase in porosity caused an increase in the permeability and the ideal combination of pore size could optimize the process[37]. It is also possible to produce heat exchangers or energy accumulators, thanks to the excellent thermal properties and the resistance of the used materials.

Also, emulsion and foam templating are widely used. Particle-stabilized emulsions and foams are particularly attractive templating process because the provide higher mechanical stability during drying and a more homogenous pore-size distribution in comparison to surfactant-stabilized systems[58]. This stems from the fact that particles are effectively irreversibly adsorbed to the air/oil-water interface, thus hindering the coalescence of the stabilized droplets.

Manufacturing 2D and 3D porous structures from particle-stabilized foams and emulsions has been explored in various studies. Aluminium foams stabilized at high temperatures by alumina and silicon are examples of 3D porous material manufactured with this technique[59]. These macro-porous materials may can exhibit open pores from 5 to 500 μ m[58] in size and total porosity varying from 45 to 98%, depending on the relative amounts of fluid in the initial mixture[60].

3.2 Porous materials obtained by Digital Light Processing

The increasing interest in the field of three-dimensional printing has led to the search for increasingly functional and innovative materials to be printed, in order to obtain functional structures for the applications for which they were designed. A printing



Figure 16 - Typical SEM images of Heterogenous Photocatalyst obtained by DLP27

technique that is gaining ground in this sector is Digital Light Processing (DLP), based on the selective polymerization, layer by layer, of a structure. The DLP method is currently used mainly for the production of 3D structures, using different types of monomers and additives to affect the mechanical properties and colour of the final printed structure[61]. Materials used for the DLP printing technique are the UV-polymerizable high internal phase emulsion (HIPE), which are converted into solid objects by UV



Figure 17 - Photograph of final structure (layer by layer photopolymerization of HIPE) (right) and SEM image of printed material (left)²⁸

radiation, and then the aqueous phase is evaporated leaving the porosity inside the structure. Li et al.[62] fabricated porous heterogenous photocatalyst by high internal phase emulsion polymerization. The resulted porous materials shows interconnected pores with an average diameter of 10 μ m and enough active moieties for photocatalysis.

Sušec et al.[63] combined additive manufacturing and HIPE printing for creating hierarchical porosity within an acrylate and acrylate/thiol-based polymer network. The key objective of this experiment is to create structures with porosity, thanks to the design using CAD software, and to add an additional level of porosity layer by layer, exploiting the characteristics of the emulsions.

According to Dong et al.[64] the solution is combining the enormous potential of the DLP 3D-printing method and the polymerization-induced phase separation. It enables formation of 3D polymer structures of highly complex geometries and spatially controlled pore sizes from 10 nm to 1000 μ m. Porous structure at the sub-micrometer scale can



Figure 18 - Photographs and SEM micrographs of (a) a printed non-porous 3D object and (b) an inherently nanoporous 3D object printed using an ink with porogens²⁹

render macroscopic objects with unique properties, including similarities with biological interfaces, permeability, and extremely large surface area, ideal for adsorption, separation, sensing or biomedical applications.

Combining Digital Light Processing and phase separation is perhaps the most used technique to create porous structures at the micrometer scale. As we have seen, this method offers many advantages, but that does not mean that there are no disadvantages. The internal porosity of the structure cannot be controlled in detail, there is inherent distribution of the pore sizes and polymer agglomerates. This can be a limitation for the mechanical points of view of the printed object.

This method can be also used to fabricate scaffolds for tissues regeneration and bones growth[65], drug delivery[66], high-performance energy storage devices[67], or connector of an electrical circuit and MEMS[61].

4. Materials and methods

The first part of this chapter describes the materials used in this thesis work. The procedures with which the different types of samples were obtained are described later. Finally, the characterization techniques used to analyze the different formulations are described.

4.1 Materials

The initial formulation contains 1,6-Hexanediol diacrylate (HDDA), a difunctional acrylate ester monomer used in the manufacture of polymers, 2-Hydroxy-2-



Figure 20 - 1,6-Hexanediol diacrylate structure



Figure 19 - 2-Hydroxy-2-methylpropiophenone structure

methylpropiophenone is a radical photoinitiator (PI), PLURONIC F-127 is a hydrophilic non-ionic surfactant of the class of copolymers known as poloxamers. PLURONIC F-127 is a triblock copolymer consisting of a central hydrophobic block of polypropylene glycol flanked by two hydrophilic blocks of polyethylene glycol (PEG). F127 has been used in



Figure 21 - PLURONIC F-127 structure

the synthesis of mesoporous materials in fact, dissolved P-123 forms micelles that are used as the backbone to make structured mesoporous materials. Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate) as radical scavenger, Disodium 2,2'-([1,1'-biphenyl]-4,4'-divldivinylene)bis(benzenesulphonate) as UV Absorber. The last two elements have been used to limit the overexposure during printing and to ensure better resolution of the printed product.



Figure 22 - Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)



Figure 23 - Disodium 2,2'-([1,1'-biphenyl]-4,4'-diyldivinylene)bis(benzenesulphonate)

4.2 Preparation of formulations

To find the formulation with the right characteristics for printing, we mixed the chemicals in various concentrations. The different formulations were prepared by combining water and PLURONIC, placed on the stirrer at 1200 rpm to obtain a correct mixing. At the end of the mixing process, HDDA and photoinitiator were added and then left for one hour in an ultrasonic bath to obtain a homogenous formulation. The different concentrations are:

HDDA (phr)	Photoinitiator (phr)	Water (phr)	PLURONIC (phr)	#NAME
100	4	50	2.5	#0.5W_25PL
100	4	75	3.75	#0.75W_375PL
100	4	100	5	#1W_50PL
100	4	150	7.5	#1.5W_75PL
100	4	50	3.75	#0.5W_37.5PL
100	4	75	5.625	#0.75W_56.25PL
100	4	100	7.5	#1W75PL
100	4	150	11.25	#1.5W112.5PL
100	4	50	5	#0.5W50PL
100	4	75	7.5	#0.75W75PL
100	4	100	10	#1W100PL
100	4	150	15	#1.5W150PL

Table 1 - Composition of 3D-printed formulations

Radical Scavenger and UV Absorber (2 phr) were added to the initial formulations to improve the control during the printing process. Formulations with these elements will be characterized with the abbreviation #RV, #UV or both.

4.3 Development of photocurable formulations

4.3.1 Photopolymerization of thin films

The prepared formulations were coated on glass slides with a thickness of 100 μ m and then polymerized with a Hamamatsu L9588-01 LC8 UV Curing Machine Spot Light Source Lightning Cure lamp with a light intensity of 25 mW / cm² and an exposure time of 10 seconds.

4.3.2 Removal of the surfactant

After the polymerization phase the slides were immersed in water for 12 hours, to remove the surfactant from the polymerized formulations and the unreacted residual monomer and put in an oven to dry at room temperature at a pressure of 100 mbar.

4.4 Printing process

The printing process used is based on the Digital Light Processing (DLP) technique, and the printer used is the Asiga MAX UV 27. The printer is controlled by a software supplied by ASIGA, ASIGA Composer, where the .stl file of the geometric structure to be printed is loaded.



Figure 24 - Asiga MAX UV 3D printer

Samples were printed with different print specifications, varying light intensity, layer thickness, exposure time and printing speed. After the printing process, samples were immersed in an ethanol bath to remove the surfactants and the unpolymerized formulations. Subsequently, samples were subjected to UV-curing to conclude the photopolymerization reaction. The print specification will be reported in details in the next chapter.

4.5 FreeCAD specification

FreeCAD is an open-source parametric 3D modeler made primarily to design real-life objects of any size. Parametric modelling allows an easy modification of the design by going back into your model history and changing the parameters. It allows to sketch geometry constrained 2D shapes and to use those as a base to build other objects. It contains many components to adjust dimensions or extract design details from 3D models to create high quality production ready drawings. FreeCAD is designed to fit a wide range of uses including product design, mechanical engineering, and architecture. In this thesis work FreeCAD was used to design structures to test the printing process and to verify the precision and accuracy of the print. A geometric structure is created with the tools provided by the software, an .stl file was exported, and uploaded on the Asiga software for the printing process.

Examples of the structures created by the software are showed in the following figures.



Figure 25 - Examples of CAD geometries designed with FreeCAD software

4.6 Characterizations methods

In this section all the characterization techniques used in the thesis work to evaluate the different chemical and mechanical properties of the liquid formulations, and subsequently of the printed parts will be described. The techniques used were:

- Ultraviolet-Visible (UV-Vis) spectroscopy;
- Photoreology;
- Infrared (IR) spectroscopy;
- Dynamic Mechanical Thermal Analysis (DMTA);
- Optical microscopy and Imaging analysis;
- Scanning electron microscopy (SEM);
- Weight loss;

- Brunauer-Emmet-Teller (BET) method;
- \circ CO₂ absorption test.

4.6.1 Ultraviolet-Visible (UV-Vis) spectroscopy

Ultraviolet-visible spectroscopy is used to obtain the absorbance or transmittance spectrum of a liquid or solid compound. The spectrum region analyzed in this experiment is between 200 - 800 nm. Tests were performed using a 6850 UV/Vis. Spectrophotometer JENWAY Single Beam.

The law governing this phenomenon is the Lambert-Beer law. A practical expression of the Lambert-Beer law relates the optical attenuation of a physical material containing a single attenuating species with uniform concentrations to the optical path length through the sample and absorptivity of the species. The expression is:

$$A = \varepsilon l c$$

where A is the absorbance, ε is the molar attenuation coefficient of the attenuating species, 1 is the optical path length in cm and c is the concentrations of the attenuating species.

In an UV-visible spectroscopy instrument a beam of light from a visible and/or UV light source is separated into its component wavelengths by a diffractions grating, then each monochromatic wavelength in turn is split into two equal intensity beams by a halfmirrored device. One beam, called sample beam, passes through a cuvette containing the solution, the other beam, called reference beam, passes through an identical cuvette without the compound. The intensity of the light beams is then measured with a detector. The light intensity of the reference beam is called I₀, and it is equal theoretically equal to the starting light intensity, despite very little light absorption. The light intensity of the sample beam is defined as I. The spectrometer scans all the component wavelengths in the interested region. Absorption can therefore be defined through two values, transmittance (T) and absorbance (A).

$$T = \frac{I}{I_0}, \quad A = \log \frac{I_0}{I}$$

If no absorption has occurred, I is equal to I_0 , then T=1.0 and A=0. If I is different from I_0 , the difference can be plotted on a graph versus wavelength. The wavelength of maximum absorbance is a characteristic value, defined as Λ_{max} .



Figure 26 - Absorbance spectrum of the common food coloring Red #3

4.6.2 Photoreology

The photoreology was used to investigate the polymerization kinetics of the compounds. The instrument is composed of: a plate-plate rheometer equipped with a UV lamp. The lower plate consists of a glass through which the light radiated by the lamp passes, the upper plate applies an oscillatory deformation to the compound. The light radiated by the lamp initiates the photopolymerization reaction, and the instrument calculates the variations in the viscoelastic behaviour of the material as the polymer chains are created. The conservative modulus (G'), linked to the elastic behaviour of the material, the dissipative modulus (G'') and their ratio, i.e. the loss factor, are measured. The experiment in our experience were conducted using an Anton Paar MCR 302 Rheometer by varying the concentration of water and surfactant within the formulation, and the polymerization kinetics of the compound were observed by adding the radical scavenger, the UV absorber, or both, to the formulation, having as a reference the process of polymerization of acrylate. The gap between the lower and upper plates was also varied, from 100 μ m to 200 μ m, to observe the light penetration and its effects on photocuring processes. The temperature was set to 25°C, a strain $\gamma' = 1$ (value chosen after a rheology test), and an angular velocity of 10 rad/s.

4.6.3 Infrared (IR) spectroscopy

Infrared spectroscopy is a technique that allows to identify the chemical bonds of materials, based on absorption in the infrared region of the electromagnetic spectrum. The infrared region of the electromagnetic spectrum can be divided into three different regions: the near-IR, mid-IR, and far-IR. The mid-IR include wavenumber between 4.000 -400 cm⁻¹, and it can be used to study the associated vibrational-rotational structure.



Figure 27 - Range of electromagnetic spectrum

This technique analyzes the behaviour of molecules excited by radiation falling in the infrared range of the electromagnetic spectrum. In this energetic range, photons are able, when absorbed, to excite the molecule in a vibrational state. There are different modes of vibration that are peculiar of each type of bond and in this way by observing the response

of the sample to an IR radiation it is possible to obtain information of the chemistry of a material.

The mechanical and physical properties of photopolymerized compounds directly depend on the degree of conversion (DC), i.e. the number of C=C double bonds breaking in the polymerized sample compared to the total number of C=C double bonds present in the initial formulation. To determine the degree of conversion in a sample composed of methacrylate, spectroscopy in the mid-IR region can be used, measuring the area subtended by the absorption spectrum at 1638 cm⁻¹, i.e. the wavenumber for the C=C bond, before and after curing. Acrylate conversion was analyzed by FT-IR spectroscopy using a Nicolet iS50 FT-IR Spectrometer equipped with attenuated total reflectance (ATR) accessory. The spectra were collected on the liquid formulation and then on printed samples. All the experiments were performed with a resolution of 4.0 cm⁻¹, averaging 32 scans for each spectrum, and 650-4000 cm⁻¹ as wavenumbers range.

4.6.4 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA allows to study the response of plastic materials when they are subjected to a dynamic or cyclic force and to accurately determine the glass transition temperature of a sample. This is done through the study of the storage modulus (G'), the loss modulus (G") and the damping coefficient (G"/G') defined as $tan \delta$. The storage modulus corresponds to the elastic response of the materials to an applied shear. The loss modulus represents instead the viscous response. The damping coefficient varies from zero for the completely elastic materials, to infinity for viscous liquids. Polymer glass transition temperature corresponds to the maximum value of the damping coefficient. In the typical DMA experiments the stress is applied at a constant frequency, the strain is kept constant and the temperature is increased at a constant heating rate.

In the experiments done in laboratory, performed with a Triton Technology instrument, frequency is fixed at 1 Hz, the temperature range is (-5 - +150) °C with a heating rate of 3°C/min, and a $\Delta x = 20 \mu m$. The analyzed samples consist in parallelepipeds with a length of 10.00 mm, a width of 9.90 mm and a thickness of 0.94 mm, printed with different concentrations of water and PLURONIC P123 within the HDDA, and a reference sample composed of HDDA only, to study how the presence of surfactant affects the mechanical properties.

4.6.5 Optical microscopy and Imaging analysis

The optical microscope Leica DFC340 FX was used to make a preliminary study on the prepared formulations, to observe the porosity in the printed structures and discharge the ones that doesn't have the "right" porosity. Images were taken with different magnifications (x5, x20 and x50). The first two magnifications were mainly used to observe the printed structure and the porosity on the surface of the structure. The larger magnification was used to see the porosity in the thin films prepared with the initial formulations with different concentrations of water and surfactant, giving out better details.

The images taken with the microscope were then analyzed with an imaging software, ImageJ, to study the average diameter size of the pore and the effective pore are with respect to the selected area. As for the most part of imaging analysis software, ImageJ allows to measure manually the dimension of every single object, in our case pore, in the pictures. Doing this particular task is quite difficult having a huge quantity of pores inside the structure, but through different passages that allows us to improve the quality of the image, is possible to use an algorithm provided by the software that auto-measures the dimensions of pores. The software recognizes every single pore, thanks to the improvement of the contrast of the image, and approximate the pore with an ellipse, measuring then the axis, the area, and the specific are of pores w.r.t the total surface area analyzed.

4.6.6 Scanning Electron Microscopy

The use of the optical microscope to characterize the microstructure of the printed object doesn't allow to see in detail inside the structure, but only on the external surface and with a low magnification with respect to the Scanning Electron Microscope (SEM). SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals derive from the electron-sample interactions revealing information about its morphology, chemical composition, crystalline structure, and orientation. SEM is mainly used for imaging. When high-energy electrons impinge on the sample surface, produce secondary electrons (SE), backscattered electrons (BSE), diffracted backscattered electrons, photons, visible light, and heat. The first two, secondary and backscattered electrons are used for imaging. Secondary electrons are most valuable for showing morphology and topography on samples, backscattered electrons are most valuable for illustrating contrasts in the composition of the sample. In the thesis experiments, SEM was used to observe with a very high magnification (till x30.000) the printed structures, to see in detail the inside porosity. The images were taken from samples that differ in concentrations and post-printing treatment.

The morphological characterization of the printed samples was carried out by Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 40). The samples were coated with a thin film of platinum.

4.6.7 Weight loss

To verify the presence of interconnected porosity that allowed the surfactant extraction, samples made purely of HDDA and others printed with the formulations containing water

and surfactant were printed. Immediately after printing, samples were weighed, subsequently placed in ethanol to remove the surfactant and the unreacted monomer, and finally placed in oven to dry for a whole night to remove any water remaining inside the structure.

To perform a quantitative analysis, the change in density of the printed parts are calculated pre- and post- the cleaning process.

4.6.8 Brunauer-Emmet-Teller (BET) method

The BET method is the most used to calculate the porosity and surface area of powders and porous structures. BET measures surface area based on gas absorption, more specifically, it allows determination of the overall specific external and internal surface area of disperse (e.g., nano-powders) or porous solids by measuring the amount of physically adsorbed gas according to the Brunauer, Emmett and Teller (BET) method. The volume of gas absorbed on the surface (nitrogen in the experiment considered) is measured at the nitrogen boiling temperature, while the pressure or concentration of the adsorbing gas is increased. At this temperature the nitrogen condenses on the surface forming a layer of single atoms, so knowing how much a single atom measures, and knowing the amount of gas absorbed, we can calculate the surface covered by the gas. A disadvantage of this technique is that the closed porosity is not reached by the gas and consequently not calculated.

The BET equation used to calculate the surface area is:

$$\frac{p}{n_a(p_0 - p)} s_{total} = \frac{1}{n_m C} + \frac{(C - 1)}{n_m C} \cdot \frac{p}{p_0}$$
Figure 28 - BET Theory equation

where n_m is the monolayer capacity, n_a the number of gas molecules adsorbed in volume units and *C* a BET constant related to the heat of adsorption.

4.6.9 CO₂ absorption test

A theme that characterizes the scientific debate in recent years is the rise in the temperature of our planet and the consequences that it can lead to over the years. The main cause of global warming, according to some studies carried out by the IPCC, is the release by humans of carbon dioxide, thus increasing the greenhouse effect.

The filters have been tested for the absorption of carbon dioxide following a treatment with soda. They were immersed in soda solutions with different molarities (0.1M and 1M), to test the absorption in relation to the two concentrations. After the treatment, the samples were dried at room temperature, in vacuum, for 48h and once dry, tested.

The test was done with the following instrument consisting of the sample chamber, two filters for water condensation, one before and one after the sample chamber. The sensor consists of a laser set to the carbon dioxide absorption frequency.

The results were then collected and manipulated using the GASLAB software, which analyzes the experiment and outputs the ppm value of the carbon dioxide absorbed during the experiment.



Figure 29 - Experimental setup for CO2 absorption test

5. Result and discussion

This chapter will report the experimental results obtained in the various experiments conducted during the laboratory experience. The goal of the thesis work is to obtain threedimensionally printed structures, composed of polymeric materials with porosity, for potential applications such as carbon dioxide capture, sensors, filters, and others. The first step was to analyze the chemical characteristics of the various formulations, to verify which were the best formulations for providing porous microstructures. Then, the chosen formulations were 3D printed, and then characterized as described in the next paragraphs.

5.1 Preliminary studies

As illustrated in the previous chapter, the first phase of the thesis work was to choose the formulations with the right characteristics, i.e., the uniformity of porosity in a photopolymerized layer. As preliminary investigation, thin films of formulations containing different amount of water (see Table 1) were coated on glass slides and UV cured at room conditions, with an UV Lamp intensity of 25 mW/cm² for 10 seconds. Those tests showed that the formulations containing a larger quantity of water with the same quantity of acrylate are not easily polymerised (#1W***, #1.5W***), resulting in brittle polymers with no consistency. Here we suppose that the large amount of water and surfactant create an inverse emulsion (oil in water), not allowing the polymer to form a uniform film but curing only in small droplets, resulting in a still liquid and viscous material.



Figure 30 - #1.5W150PL and #1W100PL thin films

After a 12-hours ethanol bath to remove the surfactant remaining inside the layer, the deposited films were observed under an optical microscope.

As can be seen from the images of the deposited films related to the #1.5W150PL and #1W100PL formulations, the polymerization did not occur uniformly over the entire surface. Many areas have not been polymerized, and the others show some porosity, but more characterized by large "bubbles" along the surface at a great distance between them. It can be said that these types of formulations do not deliver the desired result, making them unsuitable for the experiment we want to perform.

On the contrary, formulations with less water (#0.5W***, #0.75W***), after being illuminated with a UV lamp at an intensity of 20mW/cm², are perfectly polymerized, creating a homogeneous surface.



Figure 31 - #0.5W50PL (right) #0.75W56.25PL (left) thin films

As it is possible to see from the previous images, both formulations allow to have structures with internal porosity and along the entire volume. The main difference between the two formulations is the uniformity of the porosity and the size of the pores. The analyses on the dimensions were made through the imaging software ImageJ, evaluating the size of the pores through an algorithm that approximates the shape of the pores to ellipses and measures their characteristic dimensions, i.e. length of the axes and area.

This process can be divided into three phases: the first consists in modifying the selected image to increase its quality, contrast, and brightness, because the software needs a very high contrast to recognize the pores from to the rest of the surface. In a second phase, a threshold value is chosen to distinguish the pores and the rest of the surface, transforming the image in a black and white picture. The last phase consists in manually approximating the pores to ellipses and calculating their dimensions.



Figure 32 - Phases of ImageJ algorithm to calculate the dimensions of pores

As it is possible to see by comparing the images related to the different phases of the algorithm, the procedure may induce errors. Agglomerated pores are not always recognized as separate pores, or, on the contrary, surface defects are recognized as very small pores. To overcome this problem there are various solutions, such as putting a filter that eliminates those "pores" that have dimensions below a certain threshold or selecting a region of the image particularly free of defects and therefore with the possibility to be analyzed with greater precision. The results consist in an average of values taken from different images of the same formulations, calculated both through an algorithm and through a manual measurement of each pore.

FORMULATION	AVERAGE DIAMETER	
#0.5W_25PL	10.46 µm	
#0.75W_375PL	8.11 μm	
#0.5W50PL	13.38 μm	
#0.75W75PL	12.68 μm	

5.2 Polymerization kinetics and printing specifications

As described in the previous chapter, the photorheological tests allow to study the polymerization kinetics of the formulation, analysing in detail the evolution over time of the crosslinking process. These tests will give an indication of the formulations' behaviour during the printing process, for instance related to the time necessary to complete the polymerization when exposed to a certain light intensity, or to the extent of penetration of the light intensity in the formulation. Photoreology test gives as outputs G' and G ", respectively the conservative and dissipative modulus.

The storage modulus G' (G prime, in Pa) represents the elastic portion of the viscoelastic behaviour, which quasi describes the solid-state behaviour of the sample. The loss modulus G" (G double prime, in Pa) characterizes the viscous portion of the viscoelastic behaviour, which can be seen as the liquid-state behaviour of the sample.

Viscous behaviour arises from the internal friction between the components in a flowing fluid, thus between molecules and particles. This friction always goes along with the development of frictional heat in the sample, and consequently, with the transformation of deformation energy into heat energy. This part of the energy is absorbed by the sample; it is used up by internal friction processes and is no longer available for the further behaviour of the sample material. This loss of energy is also called energy dissipation.

In contrast, the elastic portion of energy is stored in the deformed material; i.e. by extending and stretching the internal superstructures without overstressing the interactions and without overstretching or destroying the material.

When the material is later released, this unused stored energy acts like a driving force for reforming the structure into its original shape.

Storage modulus G' represents the stored deformation energy and loss modulus G" characterizes the deformation energy lost (dissipated) through internal friction when flowing[68].

In the tests performed in laboratory, the results obtained from the developed formulations have been compared to the polymerization kinetics of a formulation containing HDDA and photoinitiator, to study the influence of the surfactant within them.

The graphs (fig. 33-35) show the conservative module compared to the irradiation time. The UV lamp has been turned on after 60 seconds. As we can see in the three cases analyzed by varying the flat-plate distance of the rheometer, the addition to the HDDA of





Figure 35 - Storage Modulus of formulations with a Plate-Plate Gap = $100 \ \mu m - HDDA$ (Black curve) and developed formulation (Red curve)

Figure 34 - Storage Modulus of formulations with a Plate-Plate Gap = 150 μm - HDDA (Black curve) and developed formulation (Red curve)



Figure 33 - Storage Modulus of formulations with a Plate-Plate Gap = 200 µm - HDDA (Black curve) and developed formulation (Red curve)

water and surfactant does not affect the polymerization kinetics, as it can be seen from the graphs, the slope of the curve immediately after turning on the lamp does not differ in the different cases. The storage modulus of the formulation containing water and surfactant, instead, is lower than the formulation of HDDA, due to the fact that the added surfactant contributes to give a "rubberier" nature to the formulation, that it is shown by the reduction of the average value of the conservative module.

By changing the gap from 100 μ m to 200 μ m with step of 50 μ m, we expect a delay in polymerization kinetics. This does not actually happen as it is possible to note in the following figure. The penetration of light does not significantly slow down the polymerization kinetics and the variation of the conservative module is caused by a different degree of polymerization.



Figure 37 - Storage Modulus of formulations at different Plate-Plate Gap

To investigate more in details the polymerization kinetics behaviour of the formulations, the light intensity of the lamp was decreased from 25 mW/cm^2 to 10 mW/cm^2 , at a plate-plate gap of 150 μ m, and compared with the results obtained with the previous light intensity.



Figure 36 - Storage Modulus with different UV Lamp Light Intensity

As expected, we see a reduction in the conservative modulus, but not an excessive reduction in polymerization kinetics. This means that despite the decrease in light intensity, polymerization is quite fast.

After carrying out the photoreology test, it was decided to print the first formulations. The first print test was made with the geometric structure in figure (fig. 37) applying the following printing parameters, extrapolated from the results given by the other tests.

	Value	Unit
Light Intensity	25.00	mW/cm ²
Slice Thickness	0.100	mm
Exposure Time	5	S
Burn-In exposure	10	S
Burn-In layers	2	

Table 2 - Printed specifications - 1st Test

The Burn-In exposure time is always higher than the standard exposure time. This is due to the fact that the first layers must have higher strength to support the entire weight of the structure. The drawback of increase the Burn-In exposure time is that, if it is increased too much, the adhesion between the printing platform and the base of the structure is lost, causing the fall of the entire part.



Figure 38 - CAD file of the printed object

The first printed objects are shown in figure (fig. 39). It is evident that the printing characteristics are not ideal. In the two objects we can see how the structure obtained after printing does not coincide with the desired geometry. What can be noticed is an uncontrolled polymerization of the resin, that went out and beyond the irradiated areas, causing a filling of the empty parts of the structures.



Figure 39 - First printed objects using printing specifications in Table 2

Based on the photoreology tests obtained previously, in a following set of experiments the light intensity was modified. It was decided to change the light intensity of the printer, passing from 25 mW/cm^2 to 10 mW/cm^2 . New printing specifications were:

	Value	Unit
Light Intensity	10.00	mW/cm ²
Slice Thickness	0.100	mm
Exposure Time	5	S
Burn-In exposure	10	S
Burn-In layers	2	

The second print made by decreasing the light intensity shows better results. The pillars of the structures are well defined and recognizable, although the base is still full due to excessive polymerization. Unfortunately, with these parameters only uncomplete structures were obtained. In fact, as it is possible to see, the second layer of the cube was not printed. So, decreasing the light intensity has solved the problem related to overexposure, but now but now the intensity is not enough to allow a complete crosslinking, in fact the pillars seem not to bear the weight of the second layer of the cube.



Figure 40 - Printed objects with different light intensity - 25 mW/cm² (left), 10 mW/cm² (right) Finding the right balance between exposure times, light intensity, and thickness of the printed layers for each step has allowed us to print objects with more and more precision, not completely solving the problems of filling the bases, and limiting the choice of structures to be printed to due to poor strength of the vertical pillars.

So, it was decided to add two ingredients to the formulation, namely a radical scavenger and the UV absorber. As mentioned in the previous chapter, these two elements may allow a better printing, with better resolution related to a better control of the extent of polymerization both on z direction and on x-y plan. Following the same procedure described above, photoreology tests were carried out to analyse the polymerization kinetics of the formulations by adding one of the two elements, or both, and then extrapolating the new printing specifications.



Figure 41 - UV-Visible spectra of formulations with PLURONIC and additives



Figure 42 - Storage Modulus of different formulation with Plate-Plate Gap = $150 \mu m$ and Light Intensity = $25 mW/cm^2$

It is clear that to obtain the same modulus of the formulations than without the presence of the UV Absorber and the Radical Scavenger, a higher light intensity is necessary. The explanation of this lies in the UV-Visible spectroscopy. Analysing the UV-Visible spectra obtained during the experiment, inserting the two elements inside the formulation, a peak in the spectrum appears. This belongs to a competitive absorption of light induced by the presence of UV Absorber. In this case, both the photoinitiator and the UV absorber absorb in the same spectral range, inducing a decrease of photon dose available for the photoinitiator which, in turns, lead to a decrease of photoinitiation rate and thus slower kinetics.

The graph in (fig. 42) shows how the UV Absorber and the Radical Scavenger decisively influence the polymerization kinetics of the formulation. The Radical Scavenger does not affect the final value of the storage module, in fact its use is exclusively to avoid overpolymerization in the x-y plane, in our case to avoid filling the empty spaces of the structure. UV Absorber on the other hand has a greater impact on the formulation. Its role is to absorb part of the light intensity that would otherwise be absorbed by the reactive species within the formulation causing greater penetration of light inside the structure during the printing process, influencing the previously printed layers. The combined effect of the two elements therefore helps both to limit the spreading of the polymerization outside the desired geometry, and to decrease the length of light penetration.

Looking at the graph we can extrapolate new printing specifications. Using the Radical Scavenger and UV Absorber, complete crosslinking takes place 30 seconds after the lamp is switched on, so the exposure time during the printing process must be similar. The photorheological test was performed with a gap between the rheometer plates of 150 μ m, but as we can see, the storage modulus value of the formulation containing both species is about two orders of magnitude lower than the formulation containing HDDA only. This means that even if the exposure time of the formulation is increased, the structure could not be so rigid as to support the weight of the entire object.

To get more information about the thickness of the layer to be printed and the light intensity to use, a further photorheological test was carried out to study the storage modulus trend as the gap thickness varies.



Figure 43 - Storage modulus of complete formulation at different Plate-Plate Gap

Taking into account the considerations made previously and analysing the graph of the photorheological test carried out on the complete formulation, the printing specifications have been changed, varying in addition to the light intensity, also the exposure time. The new print specifications chosen were:

	Value	Unit
Light Intensity	40.00	mW/cm ²
Slice Thickness	0.100	mm
Exposure Time	30	S
Burn-In exposure	40	S
Burn-In layers	2	

Table 4 - Printing specifications - 3rd test

As it is possible the see in the following picture (fig. 43), the printing specifications works correctly. The result obtained from the print is very satisfactory, a high accuracy is denoted, without any filling of empty or hollow parts.



Figure 44 - Printed part with the complete formulation containing UV Absorber and Radical Scavenger

5.3 Final evaluation of the printing process

Having excellent precision in the printing process means obtaining a structure that coincides as closely as possible with the CAD of the object you wanted to print. To prove



Figure 45 - TOWER CAD geometry (left) and effective printed structure (right)

the actual accuracy of the printing we used software capable of scanning the printed piece three-dimensionally and overlapping it with the CAD file of the structure, resulting in an overlay map that indicates the printing precision. The experiment was carried out on the "TOWER" piece printed with the printing specifications described in the previous chapter, which structure is reported in the next image.

The experimental setup consists of a platform on which the sample is positioned, which translates and rotates to ensure a complete image in all x, y, z directions. The image obtained is subsequently digitized, with the possibility of re-scanning the hidden parts of the structures to ensure correct scanning even in those areas.

The results obtained prove that the printing results are exceptional and that the specifications used in the printing process are ideal for the formulation we have developed. As we will see in the following images obtained by superimposing the scan to the CAD of the piece, the precision is very high, with a variation from the original piece around 50 μ m. This variation can be justified for several reasons: the precision of



Figure 46 – 3D-Scanner experimental setup

the 3D-scanner is not ideally infinite, so it is legitimate to notice imperfections; moreover, to obtain the most perfect scanning possible, the piece was coated with a powder, in order to limit the reflection of light on the white structure.



Figure 47 - Superposition of CAD geometry with the image obtained through the scansion

In the images there are areas with a high value of imprecision compared to the original CAD. These imperfections are caused by the inability of the scanner to detect the internal areas of the structure, and by the presence of the support that we had to insert to hold the object during scanning.

To further evaluate the printing precision, the software gives the possibility of sectioning the image obtained, evaluating the accuracy of the printing as the height changes, layer by layer.



Figure 48 - Section of the printed objects - Comparison between CAD and printed object

With this further analysis it is possible to state that the quality of the printing process is very satisfactory. We are able to accurately replicate very complex structures while maintaining high confidence with the original geometry.

5.4 Conversion degree of polymerized printed parts

To evaluate the extent of polymerization in the 3D printing, it was investigated the degree of conversion of the C = C double bonds after the printing process. This evaluation was



Figure 49 - IR spectrum of #0.5W50PL pre- (red) / post-(blue) polymerization

performed by studying the IR spectra. In the following figures (fig. 48, 49) the spectra of



Figure 50 - IR spectrum of #0.75W75PL pre- (blue) / post-(red) polymerization

the liquid formulations (red) are compared with the IR spectra of the printed samples (blue).

The images represent the spectra of the two formulations obtained by IR spectroscopy. The spectrum region we need to focus on is the one around the wave number 1638 cm⁻¹, which is the wavenumber related to the double bond C=C (IR Spectrum Table by Frequency Range provided by Sigma Aldrich). As a reference for the two graphs, it was decided to graphically superimpose the peaks relative to the wave number 1720 cm⁻¹, relative to the C = O double bond that it's not involved in the polymerization process. The degree of conversion is thus obtained by calculating the area subtended by the two curves at the peak at 1638 cm⁻¹ before and after polymerization, and applying the following formula:

$$\% DC = \left(1 - \frac{A_{polymerized}}{A_{liquid}}\right) * 100$$

The value of the conversion degree is an evaluation criterion for the overall properties of the printed structure, such as time stability, mechanical properties, and swelling degree. Lower is the degree of conversion. higher is the quantity of unpolymerized monomer and unreacted functional groups act as plasticizers.



Figure 51 - IR spectrum of HDDA formulation pre- (green) / post- (red) polymerization

The results obtained from the two formulations describe the characteristics of the two materials according to expectations. Using as a reference a formulation composed exclusively of HDDA and photoinitiator, as the amount of surfactant inside the formulation increases, the degree of conversion decreases. Calculation has been performed through the software OMNIC 9 and the results obtained are:

Table 5 - %DC results

Formulation	% DC
HDDA	77.36
#0.5W50PL#RS#UV	74.09
#0.75W75PL#RS#UV	73.17

This consequence can be explained by the introduction of the surfactant between the polymer chains, which limit cross-linking, reducing the degree of conversion. We can have proof of this both by observing the photoreology graphs described above, which show a reduction in the storage modulus when we insert the surfactant, and we will also
have proof of this in the next paragraph when we will look at the curves obtained from the DMTA.

5.5 Mechanical properties inspection through DMTA

Each material responds differently according to the type of stress applied and according to its nature. In our experiment three different samples were analyzed. The first, taken as reference, is a printed parallelepiped of HDDA, the others are two parallelepiped printed with the formulations developed in this thesis work, respectively #0.5W50PL#RS#UV and #0.75W75PL#RS#UV, to highlight the influence of additives on the thermal/mechanical properties of the structures.

As can be seen from the graphs in the following figure (fig. 51), the introduction of additives, i.e. water and surfactant, in the formulation with which the pieces were printed, leads to a decrease in the crosslinking density as evidenced by the decreasing modulus values with increasing the concentration of additives inside. Studying the graphs relating to the trend of the *tan* δ , a slight increase in the glass transition temperature is noted, corresponding to the peak of the *tan* δ factor. By studying the curves, we can extrapolate information about the reticular inhomogeneity. Let's see how the pieces printed with the #0.5W50PL#RS#UV and #0.75W75PL#RS#UV formulations have a wider FWHM than



Figure 52 - DMTA analysis output data

that related to the piece printed with HDDA. This means that the pieces printed with the developed formulations have a greater cross-linking inhomogeneity.

5.6 Evaluation of printed structures through SEM

The characterization techniques analyzed so far have been useful to study the printed structures from the chemical point of view of the formulations and the thermal/mechanical properties. In this section a morphological analysis will be studied. Now the study focuses on the evaluation of structures from an optical point of view. Pores in the structure have an average diameter of the order of micron, then it was decided to observe the objects through a scanning electron microscope, which provides a much higher magnification than the optical microscope and provides information on the morphology and composition of the sample. The 3D printed samples analysed are those obtained using the #0.5W50PL and #0.75W75PL formulations, to see how the amount of surfactant with the same monomer affects the internal structure of the sample.

From the images we can clearly see how the formulation with the greatest amount of surfactant induces structures with a higher porosity. Furthermore, in sample



Figure 53 - Samples (#0.5W50PL right, #0.75W75PL left) structure analysed with SEM (M=400x)



Figure 54 - SEM images (#0.5W50PL right, #0.75W75PL left) with a magnification M=700x #0.75W75PLthe porosity appears also more uniform along the entire structure than in sample #0.5W50PL.

With a higher magnification it is even clearer that the best formulation to guarantee a better porosity, and therefore a more satisfactory result, is the one with the greatest amount of surfactants. In addition to guaranteeing porosity along the sample surfaces, this also develops inside, creating channels inside the structure capable of increasing the available surface area. From the images we can see how inside the channels created, there is the presence of micro-balls. Those elements comes from vesicles of monomers formed during the emulsion process. Some of these micro-balls have a sponge structure, i.e. they are also porous, as we can see from the following image.



Figure 55 – Details of micro-balls inside the printed object

However, to increase the surface area of our objects, it is not enough to have porosity outside the structure. What greatly affects the effective area available are the internal channels that are created inside the structure, connecting the various pores. What we can



Figure 57 - #0.5W50PL structure - Details of pores' interconnection

notice by further increasing the magnification is that this connection between the pores is much more present in structures printed with the formulation # 0.75W75PL, the connection also extends into the innermost layers of the structure, which does not happen in other objects.



Figure 56 - #0.75W75PL structure - Details of pores' interconnection

The results obtained through the Scanning Electron Microscope suggest that the formulation containing a greater quantity of surfactant and water can fulfil better the requirements that were expected. This formulation allows to print objects with high precision, as happens with the other formulation with the same printing specifications but giving more distributed and interconnected porosity.

5.7 Effective porosity of the printed parts

Verifying the extent of the internal channels of the structure through the SEM is not possible. To evaluate indirectly the porosities in the structures, it was therefore decided

to print samples of pure HDDA, cubes with dimensions of 5 mm x 5 mm x 5 mm, and the same samples with the formulation studied in this thesis work.

The samples were printed and then weighed, in order to calculate the density variation between the two different formulations, the first completely full, and the second with intrinsic porosity. Nine samples were analysed for each formulation, giving the results listed in Table 6.

To perform a quantitative analysis of the experiment, the average density of the two types of samples was calculated to see how it varied between the two formulations. The formula used to calculate the density is as follows:

$\rho = \frac{mass_{sample}}{Volume}$

HDDA	#0.75W75PL
123 mg	118 mg
131 mg	112 mg
130 mg	115 mg
128 mg	121 mg
129 mg	124 mg
128 mg	120 mg
127 mg	125 mg
132 mg	126 mg
128 mg	123 mg

Table 6 - Weighted results

The results obtained verify what was shown in the previous chapters. The density decreases in the samples composed with the formulation under consideration, passing from the initial 1.027 g / cm³, to 0.963 g / cm³ in the new samples, i.e. a reduction in weight of 6%, with a Standard Deviation (σ) equal to 0.0356, that means we have a very confident result in measurement.

This shows that inside the structures are indeed empty, so the presence of the channels between the pores is verified.

6. Applications

In the previous chapters we have studied and analyzed the formulations developed from a chemical, mechanical, and morphological point of view. We have seen how thanks to the developed formulation it is possible to create structures with complex geometries with internal porosity. Being able to exploit the porosity of these structures was the goal that we set ourselves at the beginning of the thesis work, focusing our attention on the field of filters for Quality Air Filtering and for CO_2 capture.

6.1 Filters

With the FreeCAD design software it is possible to build any structure and generate the .stl file that will be sent to the printer for printing. As seen in section 4.5 FreeCAD specification, we have designed a structure composed of staggered strips, in order to recreate a filter capable of guaranteeing correct filtering of the air that passes through.



Figure 58 - CAD of printed filters

The filter was created using a Poly(ethylene glycol) diacrylate formulation, and tested as antibacterial filter, showing excellent performance.



Figure 59 - Filter printed with formulation of PEGDA

6.2 Absorption of Carbon Dioxide

To exploit the higher surface area, filters were printed with the #0.75W75PL#RS#UV formulation developed in the thesis work. The formulations was chosen due to its better porosity with respect to the other formulations. A higher porosity increases the surface area of filter available to the adsorption of carbon dioxide.

To functionalize the printed structures to the absorption of carbon dioxide, they have been treated with Sodium Hydroxide. The printed filters were immersed in two different solutions with different molarity, to study how the different concentration of Sodium Hydroxide affects the absorption. The samples were left in solution for 48h in vacuum,



Figure 60 - CO₂ absorption using filters treated with 0.1M (left) and 1M (right) solution of Sodium Hydroxide

and once dry, tested. As described in section $4.6.9 CO_2$ absorption test, results are extrapolated from GASLAB software, obtaining the following results.

The results showed how the designed filters actually absorb the carbon dioxide present in the air. The results show how filters treated with 0.1M sodium hydroxide formulation absorb more than those treated with 1M solution. Better to say, the amount of ppm absorbed per second by the two structures is almost the same, but the filters treated in solution with higher concentration absorb for less time, saturating much earlier than the other filters, as we can see in the following images.



Figure 61 – Surface area of filter without any treatment

These were the results obtained from the point of view of the absorption of carbon dioxide. Focusing now on the printed filter, analyzing the structures at FESEM, tested



Figure 62 - Surface area of filter treated in 0.1M solution

and not in sodium hydroxide solution, we see how after the treatment the internal structure of the filter changes.

The one shown in Figure 60 is the surface of the printed structure, without any treatment. Looking instead at Figure 61, we see the surface of the filter printed following the treatment in 0.1M solution. As we can see, the soda deposits on the surface of the filter, forming "leaves", which will act as a trap for the carbon dioxide particles present in the air.



Figure 63 - Surface area of filter treated in 1M solution

What we see below in Figure 62 is the surface of the filter treated in 1M solution. As we can see, the structure changes radically. The leaflets that characterized the previous surface have become agglomerates.

The surface of this sample as we can see is much more covered, a factor caused by the higher concentration of soda in the solution with which the filters have been treated. Despite a greater coverage of the surface, however, it does not positively affect the absorption of carbon dioxide by the sample, saturating much earlier than the other sample.

7. Conclusion and perspectives

In this thesis we have studied a three-dimensional printing method for the design and creation of structures with internal porosity, aimed at increasing the surface-to-volume ratio of the structure, to increase the performance of the melded pieces in the different application sectors.

In the first chapter of the thesis, an overview of the importance of the surface area available on devices and the reasons why having more surface available favours certain events was provided. Those materials that have high surface area and porosity have been described, and their evolution in the research has been highlighted, starting from simple materials such as porous carbons, up to porous materials synthesized by organic building blocks, such as crystalline metal organic frameworks (MOFs) and crystalline covalent organic frameworks (COFs). Subsequently, attention was focused on microporous polymers, a sector that in recent years has been attracting many scientists thanks to the high chemical stability that distinguishes them.

In the second chapter, the world of Additive Manufacturing (AM) was presented. After a brief introduction on the history of AM and its evolution over the years, the main methods have been described, highlighting the advantages, disadvantages, and the materials for which they are most suitable, making a distinction between metals, ceramics, and more interest, polymers. We have described in detail the Digital Light Processing (DLP) printing technique, the 3D printing technique with which the studies of this thesis were conducted, and we studied the photopolymerization process, a process that underlies the printing technique used in experiments.

Therefore, with the research we approached a sector of interest more specific and similar to that presented in the thesis work, that is the applications of three-dimensionally printed polymeric materials, first observing the structures printed with any printing technique, and then focusing on the structures printed using DLP printing technique. The internal porosity of the structures affects their physical and mechanical properties, so having a well-defined porous matrix within the structure can be a strong point. This is true in research related to the cell-discharge rate of batteries, or in the biological sector, where porosity is a crucial factor for the regeneration of tissues and organs, but stability from a mechanical point of view must also coexist. However, there are situations in which to have irregular porosity is necessary for the system to function properly. This happens when you want to design filters, membranes, or sensors. Digital Light Processing is a printing technique with which it is possible to obtain functional structures for the application for which they have been designed. Based on the layer-by-layer polymerization, it is possible to meticulously check the entire structure. Furthermore, DLP is used to combine Additive Manufacturing and High Internal Phase Emulsion (HIPE) printing to create hierarchical porosity, i.e. create structures with porosity given by the design of the object, and add further porosity present in each layer, exploiting the characteristics of emulsions.

The first experimental part of the thesis work focuses on the development and study of photocurable polymeric formulations, containing the 1,6-Hexanediol Diacrylate (HDDA), as a monomer, the photoinitiator, key element to start the polymerization during the printing process, the PLURONIC F-127, a surfactant, mixed inside the formulation to create micelles, and once the object has been printed, removed in a solvent bath to create the internal porosity. The formulations were prepared and spread on thin films, varying the concentration of water and surfactant inside, to see how it affected the porosity present

in the layers. We noticed that as the amount of water increased with respect to the monomer, the formulation was unable to be photo-polymerized correctly, due to the interposition of water and surfactant between the polymer chains. It was therefore decided to proceed with formulations containing a lower concentration of water, and by examining the samples with the optical microscope, the best results were obtained with 33 w.% and 42 wt.% of water and surfactant in the formulation, ensuring uniform porosity along the surface whole film.

The second part of the thesis work was focused on making objects using the developed formulation. The printing process includes several control parameters, first of all the printing accuracy. We have shown how to obtain a correct printing of the object, it is necessary to add other elements to the initial formulation, namely the Radical Scavenger and the UV Absorber, which allowed greater control of the printing characteristics of the structure. The structures were printed with both formulations developed, obtaining almost similar mechanical characterization results with the Dynamic Mechanical Thermal Analysis (DMTA), and the same happens with the FT-IR spectroscopic analysis, where we notice a small decrease in the degree of conversion. The real difference lies in the optical analysis of the printed pieces made through Scanning Electron Microscopy, where the different porous structure is highlighted as the concentration of water and surfactant, shows a greater and more uniform porosity throughout the object, and we can see with the right magnification, how the porosity is interconnected inside the piece, guaranteeing a clearly superior surface contact area.

Therefore, it is possible to say that the goal of creating three-dimensionally printed porous structures with photocurable formulations has been successful. The applications treated in the laboratory are illustrated in the last chapter of the thesis work. We have focused the studies on the absorption of carbon dioxide, to exploit the large surface area available to us guaranteed by the porosity, designing structures with a filter design, and testing the effective absorption rate. The printed filters, if treated with sodium hydroxide solution, are able to absorb a high quantity of carbon dioxide present in the environment.

In the near future, it will therefore be possible to produce smaller and smaller objects with three-dimensional printing methods capable of providing high performance in the field of gas absorption, air filtration from polluting, bacterial and viral particles. It will be possible to produce ad-hoc solutions for any use with few limitations and high control of the physical, mechanical, and chemical characteristics.

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