# Synthesis and Characterization of a Hybrid SiO<sub>2</sub>/PCL Material via Sol-gel Synthesis

Sara Muñana González Macromolecular Chemistry, 2022-5 Master Thesis Project



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#### Abstract:

Studies were conducted on sol-gel synthesis of a SiO<sub>2</sub> / PCL hybrid material and its characterization. PCL ending groups were modified by incorporation of acrylate functional groups for its posterior cross-linking, simultaneous to the polymerization of the inorganic phase. Experiments resulted on successful modification of PCL, as confirmed by <sup>1</sup>H-NMR spectroscopy and the synthesis of transparent homogeneous monolithic pieces with up to 20% of polymer content. The structure and composition of the material was characterized by FTIR and XRD spectroscopy and TGA analysis. Cross linking of PCL was only possible for the polymer solution, but not for the hybrid material. Without the added effects of cross - linking, the final hybrid-material proved to be too britle for the measurement of mechanical properties. Conclusions point to shrinking of the gel during drying process as a possible explanation for the apparition of cracks and further emphasize the necessity of the extra entanglement of the structure provided by cross - linking.

Theme:

Synthesis and Characterization of a hy-

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By approving submission in Digital Eksamen, each group member accepts that everyone has participated equally in the project work and that the group is collectively responsible for the contents of the report.

# Preface

I have chosen to perform the project of "Synthesis and Characterization of a PCL based Cross-Linked Organic-Inorganic Hybrid Material" as part of the fulfillment of the curriculum of the M. Sc. in Chemistry and in order to adquire, apply and expand on the theoretical and practical knowledge of macromolecular chemistry, organic and inorganic synthesis and material characterization.

The project is focused on the idea of combining an inorganic  $SiO_2$  matrix with an organic polymer to create a material with enhance properties that add to more than the sum of its components. The motivation for this study comes from the growing interest of the scientific community on composite and hybrid materials, and their potential applications on biomedical science that can improve the quality of life of many people. I hope that my contributions in this research can aid in understanding the properties of this type of material and how they are affected by their composition and preparation.

I want to give special thanks to my supervisor Assoc. Prof. Donghong Yu for the oportunity to work on this project, and for his guidance, patience and knowledge through the whole process.

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# Contents

Preface							
1	Intr	roduction					
	1.1	Problem statement	2				
	1.2	Suggested approach	2				
2	The	eory					
	2.1	Mechanical properties of bone	5				
	2.2	Glass formation via sol-gel process	7				
	2.3	Polycaprolactone	10				
	2.4	Hybrid organic-inorganic gel	12				
3	Met	ethod 1					
	3.1	General Considerations	15				
	3.2	Synthesis of PCL-A	15				
	3.3	Synthesis of $SiO_2/PCL-A$ gels	15				
4	Res	sults and Discussion 1					
	4.1	Characterization of gels	17				
		4.1.1 FT-IR	20				
		4.1.2 XRD	22				
		4.1.3 TGA	23				
	4.2	Modification of PCL	24				
		4.2.1 Characterization of PCL-A	24				
		4.2.2 Cross-linking of PCL-A	27				
5	Conclusion 2						
6	6 Outlook						

# 7 Bibliography

33

# 1 Introduction

As the increase of life expectancy has led to an aging population, the number of people suffering from diseases or fractures derived from bone deterioration has increased, and it will continue to do so in the near future. For example, around 30% of women and 15% of men aged over 50 years suffer from osteoporosis, and the number of annual cases of osteoporotic fractures is expected to reach 4.5 million cases by 2025 [1][2].

In this scenario, an increasing focus on materials for bone tissue reparation and regeneration has been adopted. For this particular application inorganic materials known as bioactive glasses have shown promising results. These degradable materials made with  $SiO_2$  or similar oxides and ceramics, have been successfully used as granulate or powder for bone and dental grafting in small defects. However, their application for medium and large tissue replacement is limited, because of their limited mechanical properties [3]. An ideal scaffold for bone regeneration has to share load with the bone and retain its structure and mechanical properties during cyclic movement patterns, and fully inorganic bioactive glasses do not yet meet these requirements due to their relative brittleness. To overcome this, a possible solution seems to be turning bioactive glasses into hybrid organic - inorganic materials combining them with polymers to enhance their mechanical properties[4].

Hybrid organic-inorganic materials can be described as composite materials at nanometric scale that combine an inorganic component with an organic or biological component. The properties of these materials do not only depend on the characteristics of the individual components, but also on the interface between them and the interactions with each other on a molecular level[5][6].

As organic compounds tend to have a low degradation temperature, being around 100 °C for pharmaceutical drugs and a few hundred degrees for most polymers, it is not possible to apply the high temperatures required to form compact inorganic

pieces of glass. For this reason methods like sol-gel processing have gained interest over the past decades. This type of synthesis can take place at room temperature and atmospheric pressure and with common organic and aqueous solvents [7]. The mild conditions of sol - gel synthesis allow exploring a broad variety of organic compounds and interactions with the inorganic matrix.

In the field of biomedical scaffolds for bone and tissue reparation, biodegradable polymers like some polyesters, polyamides and polysaccharides have drawn attention because of their great biocompatibility, safe degradation products and positive effect on mechanical properties. Polymers can be linked to the inorganic face both covalently and through weak intermolecular interactions, such as hydrogen bonding, and the ending groups can be easily modified to change their functionality. Polymer chains can also be covalently linked to each other via cross-linking to change their reactivity, mechanical properties or thermal and chemical resistance. The combination of these ideas, can improve the performance of bioactive glasses by creating a hard but non-brittle material[8][9][10].

This project aims to investigate the sol - gel synthesis of a  $SiO_2$  / polyester hybrid material and study the chemical modification of the ending groups and the effect of cross-linking on the mechanical properties of the gel for biomedical applications.

### **1.1 Problem statement**

A study of the synthesis and mechanical properties of a hybrid organic/inorganic bioglass, via sol-gel synthesis.

### 1.2 Suggested approach

The incorporation of a non-covalently bonded polymer, namely polycaprolactone (PCL), in the structure of the  $SiO_2$  gel, and the following cross-linking of such polymer, exploring the 'network within a network' concept, in an attempt to enhance the mechanical properties of the final bioglass. An schematic summary of this approach is depicted on Figure 1.1. The idea is to follow a simple easy-to-follow synthetic process that does not require high temperatures or inert atmosphere and can be carried out under mild reaction conditions. Modification commercially available polymer is preferred over in-situ polymerization of the organic phase in order to minimize reaction times and number of variables to control.



*Figure 1.1:* Representation of the  $SiO_2$  gel network (a)) with the integration of PCL-DA (b)) and after the crosslinking of the polymer (c))

2 | Theory

### 2.1 Mechanical properties of bone

When a material is designed for biomedical applications, the desired properties of such material closely resemble those of the biological components they are attempting to replicate. In the case of bone this becomes specially tricky due to its anisotropic nature. Cancellous bone (such as the radius or the femur) is made of individual fiber-like structures known as trabeculae. Therefor the bone has a material stiffness for each trabecula, and a structural stiffness that also depends on the alignment of these fibers. For this reason, mechanical tests are highly dependant on sample geometry and orientation. (For example, the tensile strength of a femur in longitudinal direction can double that of the same bone in transversal direction) [11]. There are multiple ways to measure and describe the mechanical properties of a material, as the ability of the material to absorb the energy caused by load or impact and its post-yield reaction (elastic or permanent deformation or formation of micro- and macro-fractures) varies depending on its structure and bonding. In brittle materials such as ceramics or glass, macroscopic plastic (permanent) deformation is almost non-existent, so the strength and toughness measurements by tension or compression give a general idea on the material's resistance to fracture, but this is highly governed by the presence and size of pre-existing defects [12].



*Figure 2.1:* Schematic representation of stress distribution in compressive mechanical testing for *a*) a perfectly aligned sample and *b*) a misaligned sample

In order to minimize the effect of defects to only the ones that are intrinsic to the material, some geometrical requirements of the sample must be fulfilled. Homogeneous samples, large enough to be treated as a continuum (typically 7-20 mm in width) are required, usually in the shape of cubes or cylinders are commonly used [13]. For compression tests, the faces of the sample should be completely parallel and uniform, as even a small misalignment can lead to large stress concentrations not homogeneously distributed along the sample that cause an underestimation of the Young's modulus and strength measurements (Figure 2.1).

Among the mechanical properties an ideal material for biomedical implants should have, the ability to sustain cyclic loads is one to be considered. Metals, such as stainless steel, cobalt and especially titanium have been used for prosthetic and biomedical scaffolds because of their good load bearing abilities. The disadvantages of using metals come from their long-term toxicity (due to the release of metallic ions) and their poor adhesion to living tissue and their high thermal and electrical conductivity [14][15]. Bioceramics, such as aluminum, titanium and zirconium oxides, have been used for surgical implants for their good strength, inert behaviour and minimum thermal and electrical conductivity. However, even though they often exhibit a high elastic modulus and can withstand great stress loads before fracture, ceramics often fail at sharing the load with the bone when subjected to cyclic loads, as they are considered to be brittle materials [4]. In order to try to overcome this, hybrid materials combining bioglass or bioceramics and organic polymers are being researched for tissue engineering. This type of materials could potentially be tough and durable, maintaining the high biocompatibility and low cytotoxicity required for biomedical applications. Bone itself is considered to be a hybrid organic-inorganic material. It is a composite material formed by the mineral hydroxyapatite ( $Ca_10(PO_4)_6(OH)_2$ ) and the organic protein collagen [16]. Combining organic and inorganic compounds in one material comes with the challenge of finding a suitable synthesis process that takes into account the different processing conditions of each of the components. Incorporating a polymer in a glass or ceramic matrix could improve its mechanical properties regarding elasticity and durability, but the high temperature required for traditional processing of oxides such as SiO<sub>2</sub> is incompatible with the low decomposition point of the polymer. For that reason, alternative synthesis processes such as sol-gel processing are being considered for the creation of this type of hybrid materials.

# 2.2 Glass formation via sol-gel process

Glass and ceramics have often been used for biomedical applications due to their mechanical properties and chemical stability. However, their main limitation of these materials is that high temperatures are usually required for their processing, which is highly incompatible with the use of drugs or organic polymers that would decompose at such temperatures. Sol-gel is a process (discovered in the mid XIX century and further developed during the XX century) that allows the synthesis of amorphous inorganic materials at room temperature. The solid material is formed from soluble molecular precursors in an aqueous or organic solvent (referred as "sol") that condense into a solid gel following an inorganic polymerization reaction [17][18].

Apart from the differences in the experimental conditions, physical differences in the final product for melt- and sol-gel glasses are also noticeable. Due to the nature of the sol-gel synthesis, these glasses tend to have an inherent nanoporosity, whereas glasses obtained by melt-quenching are dense. This results in sol-gel glasses having an specific surface area two orders of magnitude higher, which directly affects properties such as bioactivity, solubility or mechanical properties. The porosity of this type of materials originates from the process by which the gel is formed. The hydrolyzed alkoxide precursors link together via condensation reactions and, since the monomer is tetrafunctional, they can form a three-dimensional network when they polymerize. The solvents and liquid components that participate in the sol-gel process are trapped in the capillaries of the structure as the gel forms. After drying, when the liquid is removed, pores are formed [19].

For the synthesis of  $SiO_2$  gels, organic precursors known as alkoxysilanes are used as starting material, and the reactions are catalyzed by a mineral acid or base. The main reactions occurring during this process are hydrolysis and both water and alcohol condensation, with the inverse of these reactions also taking place simultaneously (Figure 2.2) [20].



Figure 2.2: Scheme of reactions occurring during the sol-gel process of SiO<sub>2</sub>

Tetraalkoxysilanes are traditionally produced by reacting tetrachlorosilane with anhydrous alcohol and are water immiscible, so EtOH is usually added as a homogenizing solvent, even though the alcohol produced by the hydrolysis and alcohol condensation reactions is usually enough to act as a homogenizing agent. Alcohol also participates in the reverse reactions of hydrolysis and alcohol condensation (namely esterification and alcoholysis), so it could influence the gel forming times [20].

Regarding the catalyst, acid-catalysis usually leads to the formation of of weakly branched polymeric gels, while base-catalysis produces condensed particulate gels, as seen on Figure 2.3. After drying, this pH dependence can also be observed in the final pore-size of the xerogels, as acidic conditions lead to dense microporous (pore size < 2 nm) networks and alkaline or neutral conditions lead to mesoporous gels. For this project, since the aim is to create monolithic solid gels, the process was carried out at low pH values below the zero charge point of silicic acid (pH < 2), where we get into a metastability region with long gelation times and the



polymerization is proportional to [H<sup>+</sup>] [17][20].

*Figure 2.3:* Polymerization / growth of particles of SiO<sub>2</sub> according to pH

Under these conditions the mechanism of the reaction is likely to follow a first protonation step of the alkoxide (withdrawing electron density from Si and making it more susceptible to be attacked by water) followed by an  $S_N 2$  type substitution reaction (Figure 2.4) [20].



Figure 2.4: Scheme of a possible SN2 mechanism for the hydrolysis reaction of SiO<sub>2</sub>

### 2.3 Polycaprolactone

Polycaprolactone (PCL) is a linear, semi-crystalline, aliphatic polyester that has been drawing attention in the fields of biomedical 3D printing and tissue engineering. It can be synthesized by the ring-opening polymerization of  $\varepsilon$ -caprolactone [21]. Some properties of PCL such as, viscosity or melting point depend on its molecular weight. For example, high molecular weight PCL (80 kDa) is a white solid with a T<sub>g</sub> of 60 °C, while low molecular weight PCL (0.53 kDa) is a transparent liquid at room temperature [22].

One key reason why this polymer is being studied for medical applications is its biodegradability. This property is determined by the structure of the repeating units. Polyesters, that have similar structures, such as polyglycolide (PGA), polylactic acid (PLA), polyhydroxibutirate (PHB) or polycaprolactone (see Figure 2.5), degrade as their ester bonds undergo hydrolysis by reacting with water. A longer alkyl chain makes the polymer less hydrophilic, which leads to a slower degradation rate. Due to the longer degradation times, PCL has greater potential for its use in implants or synthetic organs [23].



Figure 2.5: Structure of various biocompatible/biodegradable polyesters

A way to further prolong the degradation time of the polymer, and enhance its mechanical properties at the same time, is cross-linking. By cross-linking, molecular freedom is decreased as the polymeric chains are linked together through covalent or ionic bonds. Some of the changes of properties that come with cross-linking include, insolubility, swelling and loss of flow properties in favour of reversible deformation [24]. Chemical cross-linking is usually triggered by the formation of free radicals, often caused by the decomposition of an initiator, which can be thermal or light-induced. Cross-linking reaction is characteristic of vinyl-polymers, because it requires the presence of double bonds. However, non-vinyl polymers like PCL can have their ending groups modified to include a double bond.

The modification of the end groups of polyesters can be carried out by a nucleophilic substitution in basic media, using some acid chloride containing a vinyl group, for example acryloyl chloride. As it can be observed on Figure the modification of the ends for polymers like PLA or PCL is usually preceded by the aforementioned ring-opening polymerization and the inclusion of a water soluble, hydrolytically labile copolymer, such as polyethylene glycol (PEG) [23][25].



Figure 2.6: Reaction scheme for ing opening polymerization and end group modification of PCL

# 2.4 Hybrid organic-inorganic gel

Organic-inorganic hybrid materials can be defined as multicomponent composite materials, whose final properties do not simply result from the sum of its components, but also the interactions and forces at the interface between both domains. This interface plays an important role in altering a number of attributes such as optical or mechanical properties, catalysis or separation abilities and chemical or thermal stability. For this reason, the general criteria to classify hybrid material, is centered around the interactions occurring at this interface. Hybrid materials are usually divided in two families: in Class I hybrids the interactions between the organic and mineral faces are weak, those being, for example, Van der Waals forces, H-bonding or electrostatic interactions; whereas in Class II hybrids the organic and inorganic components are chemically bonded by strong interactions such as covalent or ionocovalent bonds [7][26][27].

In this project, the aim is to form two polymeric networks (organic and inorganic) that intertwine each other without covalent bonding, forming a so called interpenetrating network (IPN). The interactions between the organic and inorganic matrices would mostly consist of H-bonding between the carbonyl groups of PCL and the -OH groups of SiO<sub>2</sub> formed by hydrolysis (Figure 2.7, so this material would fall into the category of Class I hybrids.



Figure 2.7: Example of H-bonding in a simple SiO<sub>2</sub>/PCL hybrid

Even though it is possible to polymerize the organic and inorganic components of the hybrid material simultaneously (by using a catalyst that is suitable for both polymerization reactions), this results in a competitive process controlled by the type and amount of catalyst and the reactivity of the monomer. In this scenario, if the inorganic network is formed faster than the organic, there is not enough space for the polymer chains to grow because of the steric restriction, resulting in the formation of shorter oligomeric chains, as seen on Figure 2.8. For this reason, the formation of the inorganic domain is usually postponed to the polymerization of the organic components [28][29].

The most direct route to form hybrid organic-inorganic materials via sol-gel process is to carry out the sol polimerization reactions (hydrolysis and condensation) in the presence of a pre-formed organic polymer, so both networks interpenetrate on a molecular level. This synthesis plan, while it is simple, it presents its own set of challenges, as in order to get homogeneous and optically transparent gels, it is necessary that no phase separation occurs in the solution containing the SiO<sub>2</sub> and the polymer.



*Figure 2.8:* Schematic representation of a hybrid organic-inorganic material, where a) the inorganic network was formed a) fast or b) slow

Considering that, one important parameter to control is the solvent. SiO<sub>2</sub> hydrolysis and condensation reactions generally take place in EtOH, where the alkoxysilane precursors are dissolved, and the mineral acid catalyst is usually added as an aqueous solution. Organic polymers, and specifically for this case polyesters like PCL, have a very poor alcohol and water solubility, and many organic solvents where the polymer can be completely dissolved, such as chloroform or dichloromethane are not miscible with water. On top of that, water and alcohol are by products of the reactions involved in the sol-gel process, which can change the composition of the solution, causing precipitation of organic compounds that were initially soluble at later stages of the reaction. In order to control the solubility issue, a co-solvent is usually added. This solvent acts as a homogenizing agent, by being able to dissolve the polymer while being miscible to some extent with water and alcohol. Some of the solvents used in sol-gel synthesis for this purpose are dimethoxyethane (DME), formic acid (FA), acetic acid (AcOH), methylacetate, dimethylformamide (DMF) or tetrahydrofuran (THF), which is the one selected for this project [5][30].

3 | Method

### 3.1 General Considerations

Polycaprolactone (PCL), tetraethyl orthosilicate (TEOS), acryloyl chloride, diethyl ether and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma Aldrich.  $\alpha$ ,  $\alpha$  azoisobutyronitrile (AIBN) was purchased from Fluka. All the reagent grade chemicals were used as purchased, without further purification.

Sample structure was characterized by Fourier transform infrared spectroscopy (FTIR, Bruker Equinox 55, 0.5 cm-1 resolution) and powder x-ray diffraction (XRD, Bruker, D8-Advance x-ray diffractometer, Cu-K $\alpha$ ,  $\lambda$  = 1.5406 Å). Sample composition was analyzed by thermogravimetric analysis (TGA, Thermal Lab SDT650, 10,00 °C/min to 600,00 °C, Gas = Nitrogen; Ramp 10,00 °C/min to 1000,00 °C, Gas = Oxygen). Structure of modified polymer was also analyzed by <sup>1</sup>H-NRM nuclear magnetic resonance spectroscopy in CDCl<sub>3</sub>.

## 3.2 Synthesis of PCL-A

10g of PCL were dissolved in CH2Cl2 at room temperature. 0.5 mL triethylamine and 0.6 mL acryloyl chloride were added, and the reaction was stirred in an ice bath for 24h. Acrylated polycaprolactone (PCL-A) was collected as a white solid by precipitation in diethyl ether and vacuum filtration, and then washed with Mili Q water.

### 3.3 Synthesis of SiO2/PCL-A gels

 $SiO_2/PCL-A$  gel samples containing 0, 5, 10 and 20% (wt) of polymer were prepared using a sol-gel method. "Sol A" was prepared by dissolving PCL-A in 16mL of THF at room temperature. "Sol B" was prepared by mixing 12 mL of TEOS and 10 mL of THF with the corresponding amount of HCl (1M) aqueous solution and EtOH and stir it vigorously for 30 min. The final sol was prepared by mixing "Sol A" and "Sol B", adding the AIBN photoinitiator (3 mg) and EGDMA and stirring the mixture vigorously for 10 min and then casting it into a mold to let it gel. The composition of the various sol samples is shown on Table 3.1.

PCL-A%(wt)	mL EtOH	mL HCl (1M)	mL EGDMA
0%	10	3	0
5%	10	3	0.2
10%	10	3	0.4
20%	10	3	0.8
0%	5	3	0
5%	5	3	0.2
10%	5	3	0.4
20%	5	3	0.8
0%	5	5	0
5%	5	5	0.2
10%	5	5	0.4
20%	5	5	0.8

Table 3.1	Composition	of SiO <sub>2</sub> /	PCL-A s	ol samples
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# 4 Results and Discussion

# 4.1 Characterization of gels

After an average gelation time of 13 days, solid, transparent and homogeneous gel samples were obtained. Changes in the amount of HCl and EtOH seem to have no significant influence on gelation times as all the samples solidified in 11 - 16 days and no evident composition related tendency. As it can be seen on Figure 4.1, during the drying process, as the solvent left the cavities of the structure, cracks formed on the gels, most prominently on the surface. These cracks kept expanding on a time until the monolithic samples broke into smaller pieces. As mentioned before in Section 2.1, mechanical testing and more specifically compression or tension tests. (This would provide information about the general mechanical properties of the material. It also matches the stress conditions the final product would be exposed to more closely than, for example, impact or indentation testing) have certain size and geometry requirements that could not be fulfilled with these samples as they would crumble during the sample preparation process (cutting and sanding) due to their low crack resistance.



*Figure 4.1:* Representative SiO<sub>2</sub>/PCL-A gel samples containing 0% (a1 and a2), 5% (b1 and b2), 10% (c1 and c2) and 20% (d1 and d2) wt. PCL-A

These results made evident that, even though the low reaction temperatures of the sol-gel process allow the inclusion of polymers or other organic phases within the gel structure, this method presents what could be considered a disadvantage compared to the traditional melt processing of SiO<sub>2</sub> which is that the materials obtained via sol-gel process are porous. This directly affects the mechanical properties of the final gel. It is possible to control the size of the pores by changing the pH, but even though the gels formed in acidic pH are theoretically more dense and with a smaller pore size than those prepared under alkaline conditions, it is still difficult to obtain crack-free monoliths of more than 1-2 cm diameter. The cracking might be caused by two main reasons: rapid or non-homogeneous shrinking during the drying process or the evaporation of solvent or products of the condensation reaction trapped in the pores. Vapour must travel to the surface of the material via the interconnected pore network, which can cause capillary stresses that can lead to crack formation. Other possible cause is the surface tension at the liquid-gas interface in the pores of the wet gel. Minimizing the effects of these phenomena can only be done at atmospheric pressure by the very slow evaporation of the volatile components [4][31]

This was attempted in this synthesis by having the gels form and air-dry in PPT containers covered by Parafilm with small holes that would allow for the slow release of these volatile components. However, even though it was possible to

determine that the gel had become solid without opening the container, it was not possible to monitor the drying process, and removing the Parafilm to recover the gel before it had completely dried would lead to crack formation because of the sudden change at the liquid-gas interface in the pores of the material.

For a similar reason, faster alternative drying methods such as freeze-drying were not used. It was initially considered, not only because it would reduce the processing time notoriously, but because the absence of a liquid during drying could reduce the shrinking of the gel and therefor the apparition of cracks. Research has shown, however, that the rapid cooling still causes cracking because of the formation of ice microcrystals [32].

As the mechanical tests could not be carried out, any assumptions about the potential mechanical properties of these hybrid  $SiO_2/PCL$  gels are merely hypothetical. Information about the properties of the two main components of the hybrid separately can be found in the literature.  $SiO_2$  xerogels and aerogels exhibit almost no plastic deformation and their elastic modulus (E) and yield strength ( $\sigma_y$ ) are highly dependant on the bulk density and porosity of the material. Changes of up to various orders of magnitude have been reported when comparing highly porous dried gels (bulk density < 0.5 g/cm<sup>3</sup>) with the more dense ones (bulk density 1 - 2 g/cm<sup>3</sup>). SiO<sub>2</sub> gels can have E values ranging from 100 to 100000 Mpa and  $\sigma$  values from around 1 to 100 MPa [33]. On the other hand, bulk PCL has an average elastic modulus of 450 MPa for both compression and tensile tests with a yield strength of 18 MPa. Unlike the amorphous SiO<sub>2</sub>, the polymer exhibits both elastic and plastic deformation. A yield strain ( $\varepsilon_{\nu}$ ) of up to 400% of the initial length has been reported. After that point, PCL exhibits large plastic deformation. Some variations in the absolute values are expected, as the measurements reported in the literature were obtained from polymer samples with an average  $M_W$  of 84,000 Da, which differs from the one used in this project ( $M_W = 14,000$  Da), but it is probably safe to assume that the PCL used here has a similar profile regarding elastic and plastic deformation) [34].

However, even though it can be deduced that the properties of the hybrid material are going to take influence from both of its components, it is more complicated to predict the overall mechanical properties of the final gel, because the properties of composite materials do not only depend on the properties of its individual components, but also the phase morphology and interfacial properties. Incorporating the polymer early on in sol-gel process has been done with the intention of having a high degree of mixture and interpenetration between the two phases, as an attempt to increase the interfacial interactions and "blur" the interfacial zone. A characteristic that was observed in the SiO<sub>2</sub>/PCL gels that were synthesized is that they were transparent. This could imply that the domain sizes are in a very small scale, as nanocomposites that showcase a deeply intimate entanglement of their components are often highly transparent, but further experimental research would be needed for this hypothesis to be confirmed [5]. Considering that the intefacial interactions (namely the H-bonding between the hydrolyzed SiO<sub>2</sub> and organic PCL) are weaker interactions than the covalent bonding occurring within each of the components, having a high degree of interpenetration could be beneficial for the mechanical properties of the final product, as having the weaker interactions more homogeneously distributed throughout the material could reduce the probability of having zones with a high concentration of defects, that could lead to critical flaws and consequent fracture.

Ideally, the inclusion of PCL in the  $SiO_2$  matrix would provide some elasticity to the material, derived from the ability of the polymer to deform under stress (both elastically and plastically), while retaining a relatively high elastic modulus; in order to have a material that is still strong and can withstand enough stress for its application as a biomedical scaffold, but it is not as brittle as SiO<sub>2</sub> alone. As none of the samples obtained were suitable for mechanical testing, it was not possible to compare them in order to observe the effect of the addition of PCL. Giving that the cracks formed mostly during the drying process of the gel and were related to the evaporation of the volatile components, it is more likely that, in this case, the macro- and macro- structure of the material (this being the porous structure caused by the solvents and liquid components that participate in the solgel process trapped in the capillaries as the gel forms) played a more important role in the mechanical properties than the interactions occurring at nanometric or molecular level between the organic and inorganic phases, thus giving a brittle material. This is, however, speculative, only based on the information provided by the literature and the observation of the behaviour of the gels during drying and sample preparation, and it is yet to be confirmed experimentally, after a proper optimization of the drying process and a study on the porosity of this hybrid [5].

#### 4.1.1 FT-IR

Figure 4.2 shows the infrared spectra of the  $SiO_2$  gel samples containing 0, 5, 10 and 20% of PCL-A modified polymer. The bands at 1080 and 470 cm<sup>-1</sup> correspond to the bending and stretching modes of the  $SiO_2$  tetrahedra. When comparing the spectra of the samples, it can be observed that there are two bands at 2920

and 1730 cm<sup>-1</sup> that are not present in the SiO<sub>2</sub>/PCL-A 0% samlple, but appear on the infrared spectrum for PCL-A (Figure 4.3). These bands, which can be attributed to the symmetric stretching of -CH<sub>2</sub>- and the stretching of the carbonyl bond, increase their intensity as the PCL-A concentration of the sample increases, confirming the presence of the polymer. The broad band at 3300 cm<sup>-1</sup> suggests hydrogen-bonding, which would match the non-covalent bonding of a Type I hybrid material according to the Judestein et al. classification [26]. But, since this band is also present in the sample that does not contain the polymer, this hypothesis can not be totally confirmed.



Figure 4.2: FT-IR spectra of (a, b, c, d) SiO<sub>2</sub> / PCL-A (0, 5, 10 and 20 % wt) gels



Figure 4.3: FT-IR spectra of polycaprolactone

#### 4.1.2 XRD

Figure 4.4 shows the XRD spectra of the  $SiO_2$  gel samples containing 0, 5, 10 and 20% of PCL-A modified polymer. It matches the signal of an amorphous material with no identifiable peaks from any crystalline structure. The amorphous structure is not visibly altered regardless of the amount of polymer added.



Figure 4.4: XRD spectra of (a, b, c, d) SiO<sub>2</sub> / PCL-A (0, 5, 10 and 20 % wt) gels

#### 4.1.3 TGA

Thermal stability and composition of the air-dried gel samples was analyzed by TGA. TGA curves for SiO<sub>2</sub> / PCL-A 0%, 5%, 10% and 20% hybrids are depicted on Figure 4.5. The degradation curves show two degradation steps for all the samples except the one containing no PCL. The first step starts roughly at 100 - 120 °C and could be attributed to the evaporation of water, solvent resudues or volatile components. The second step begins at 350 - 400 °C and matches the decomposition point of PCL. This second step is also not present in the sample with 0% polymer content, so it is safe to assume that it corresponds to the degradation of PCL. As for the 5%, 10% and 20% samples this step involves a weight loss of 7,5%, 12,8% and 21% respectively, which indicates that no significant polymer mass was lost during the synthesis. The final residue, of 72.5% (SiO<sub>2</sub>/PCL-A 0% sample), 70.9% (SiO<sub>2</sub>/PCL-A 5% sample), 66.8% (SiO<sub>2</sub>/PCL-A 10% sample) and 60.2% (SiO<sub>2</sub>/PCL-A 20% sample) would correspond to the SiO<sub>2</sub> residues of the inorganic network.



Figure 4.5: Thermogravimetric analysis curves of of SiO<sub>2</sub> / PCL-A 0, 5, 10 and 20 % wt) gels

# 4.2 Modification of PCL

#### 4.2.1 Characterization of PCL-A

In order to confirm that the reaction had proceeded and the end groups of the polymer had been modified, the product was characterized by <sup>1</sup>H-NMR spectroscopy. The spectra for unmodified PCL and modified PCL-A are shown in Figures 4.6 and 4.7.



Figure 4.6: <sup>1</sup>H-NMR spectrum of PCL



Figure 4.7: <sup>1</sup>H-NMR spectrum of PCL-A

For the commercially available PCL, the spectroscopic data contains the following peaks for <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  [ppm]: 4.08 (t, J = 6.6 Hz, nH, H1), 2.33 (t, J = 7.8 Hz, nH, H2), 1.67 (m, 2nH, H3 and H5), 1.41 (m, nH, H4).

The modified PCL also contains the same strong peaks as the starting material (indicating that the monomer structure is the same). Additionally, it contains the following small peaks for <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  [ppm] :6.42 (dd, J= 17.3 Hz and 1.3 Hz, 1H, H<sub>a</sub>), 6.14 (dd, J= 17.3 Hz and 10.5 Hz, 1H, H<sub>b</sub>), 5.84 (dd, J= 10.5 Hz and 1.3 Hz, 1H, H<sub>c</sub>). These signals correspond to the protons of the acrylate group.

Figure 4.8 shows the possible structures for PLA and its modifications. As linear PCL has two different ending groups with different reactivity (-COOH and -OH), the final product could have one acrylate end, two of them, or be a mixture of both molecules.



*Figure 4.8:* Schematic molecular structures for polycaprolactone (PCL), monoacrylated polycaprolactone (PCL-MA) and diacrylated polycaprolactone (PCL-DA)

The integration of the peaks shows that the relative intensity matches that of an average acrylate group : monomer ratio of 1 : 125, which can be indicative of the modification of one of the ending groups of the PCL chain (Mw(PCL) = 14000 g/mol).

The suggested reaction mechanism is a slow deprotonation step in basic media (Eq. 1), followed by a fast SN2 substitution reaction (Eq. 2). Giving the higher reactivity of the carboxylic acid over the alcohol group, it is more likely that this is the reactive end that was modified, leading to the final mono-acrylated polycaprolactone structure (PCL-MA).



Figure 4.9: Reaction mechanism for the modification of PCL

#### 4.2.2 Cross-linking of PCL-A

In order to confirm the presence of cross-linkable double bonds, the polymer was dissolved in THF and heated to 70°C, a temperature at which the AIBN initiator decomposes (AIBN can start decomposing at temperatures above 42°C, but it is typically heated to 66 - 72 °C when it is used to initiate reactions in a laboratory setting [35]), and the change of properties after the cross-linking process was observed.

The solubility of the material, as well as the modified and unmodified starting materials (PCL and PCL-A), was tested in common organic solvents, and the results are shown in Figure for comparison. As expected, none of the samples was soluble in a non-polar solvent like n-hexane, and they were not soluble in acetone either. But when two of the solvents typically used to dissolve polymeric compounds, namely tetrahydrofurane (THF) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), were used, both PCL and PCL-A dissolved but the cross-linked sample remained insoluble.



*Figure 4.10:* Solubility test at room temperature for PCL, PCL-A and cross-linked PCL-A in a) THF b)  $CH_2Cl_2$  *c)* acetone and *d*) *n*-hexane

However, even with a successful modification of the polymer with the addition of cross-linkable double bonds, the conditions for the decomposition of the chosen initiator AIBN (heating over 60°C) interfere severely with the sol-gel process, as it would lead to a potential change of the reaction kinetics and variables like fast evaporation of the solvent would be difficult to control. And taking into account

that without the cross-linking of the polymer network it was not possible to get a gel sturdy enough for mechanical testing, it is imperative to find a way to enable simultaneous cross-linking and gelation.

A possible solution would be the use of ultraviolet light with a photoinitiator to trigger the cross-linking process. This process has been used successfully for cross-linking of similar modified polymers, using photoinitiators such as camphorquinone (CQ)[16]. AIBN was also tested as a photoinitiator, but after 3h of exposure no visible changes were observed on the PCL-A solutions, so it was decided to use heat to initiate the reaction instead.

# 5 Conclusion

This project aims to synthesize a non - covalently bonded hybrid  $SiO_2$  material by sol - gel synthesis. It also studies the modification of the ending groups of the polymer for the inclusion of acrylate functional groups, that allow for crosslinking of the organic component, which, if triggered to occur simultaneously to the polymerization of the  $SiO_2$  inorganic matrix, would lead to a superior level of network entanglement, thus potentially improving the mechanical properties of the material. Polycaprolactone (PCL) was chosen as the organic component for its biocompatibility and slow degradation to innocuous organic compounds as well as its commercial availability and easy modification.

Even though it was not possible to cross-link the polymer during the sol - gel process due to the incompatibility between the conditions for the decomposition of the chosen initiator and the conditions of the gelation process, it was possible to create transparent homogeneous solid gel samples that incorporated up to a 20% of PCL content in their structure. The final material, however, proved to be too brittle for mechanical testing. This, together with the structural analysis of the gels, suggests that the interactions between the different components are relatively weak, thus classifying this material as a Class I hybrid. Since the amount of polymer that can be incorporated is limited by its solubility in the solvent mixture, the brittleness of the material further emphasizes the need for the study of the effects of cross-linking, which is left for future research.

On the other hand, modification of PCL was successfully achieved by acrylation of the ending -OH groups. Characterization by H<sup>1</sup>-NMR, suggests the modification of one of the ending groups, but it is yet to be confirmed which functional group reacted or if it is a mixture of various products. Modified PCL-A was cross - linked with EGDMA in the presence of AIBN and heat was applied to trigger the reaction. The change of properties after cross - linking was confirmed by solubility tests.

The long gel formation times and lack of a unified and standardized procedure for sol - gel synthesis to follow, as well as the many variables (solvents, sample volume, stirring time, exposure to air...) to control, with not enough information of their effect on the polymerization and gel formation process, limited the number of samples that were successfully prepared. For that reason, it might be to early to draw any definitive conclusion about the viability of this product and its performance as a material for bone tissue reparation or regeneration.

# 6 Outlook

The long time required for the optimization and sample synthesis restricted the time available for studying the cross - link process of PCL. This would be the first and most necessary task to carry out in future research, as, even though the formation of homogeneous hybrid gels and the modification and cross - linking of the polymer have been successfully carried out separately, it is yet to be explored the viability of the simultaneous inorganic polymerization and organic cross - linking seems to be the path to follow in this regard, so an in-depth study with a variety of photoinitiators on the effect of UV light exposure times and radiation intensity on both the polymer and the hybrid material could be a promising starting point.

Another important task, given the potential applications of this type of material, would be the study of mechanical properties. A variety of tests such as Vickens indentation for hardness, Charpy V-notch for toughness, compression for tensile strenght or load cycle fatigue tests for durability, would provide crucial information on its performance and potential uses.

Polycaprolactone was the chosen polymer for this study, but other biodegradable or non-degradable but biocompatible polymers could be studied and compared in terms of performance, safety and cost.

The ultimate goal would be reaching the point where the material is physically and chemically stable enough to start making *in-vitro* and *in-vivo* studies to test its viability and effect on human bodies.

# 7 | Bibliography

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