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**Formulation of sodium borosilicate glass inks from ceramic precursors for Direct Ink Writing**

**Formulación de tintas de vidrio de borosilicato de sodio a partir de precursores cerámicos para Escritura Directa de Tinta**

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*Eppur si muove*

Galileo Galilei

I wanted to write this at last, the fact I am doing it right now marks the end of one stage in my life and the beginning of a new one. To be honest, this has been a longer than expected journey, yet, I could not be happier with it. The list of people I would like to thank is so big it could fill the entire thesis by itself, however, I want them to know I appreciate every single second of their time. The support you have given me made me overcome harsh times and keep moving forward through wind and storms. Thank you all for always been there.

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**REPORT**



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# 1. GLOSSARY

AM	Additive Manufacturing
CAD	Computer-Aided Design
DIW	Direct Ink Writing
FDM	Fused Deposition Modeling
LDM	Low-temperature Deposition Modeling
NBS	Sodium borosilicate
TEOS	Tetraethoxysilane
NaOEt	Sodium ethoxide
TMB	Trimethyl borate
EtOH	Ethanol
PLU-F127	Pluronic-F127
PPO	Polypropylene oxide
PEO	Polyethylene oxide
IR	Infrared spectroscopy
FTIR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence



## 2. SUMMARY

Additive manufacturing (AM) refers to a series of techniques in which, in contrast to traditional manufacturing techniques, the final pieces are achieved by adding material instead of subtracting it. These technologies have been developing for more than 25 years and they are also referred to as Rapid Prototyping, Freeform Fabrication, Layered Manufacturing, 3D Printing and others, being all synonyms. By using these techniques, complex shapes can be produced with practically any material, allowing virtually infinite applications for AM techniques.

The way the material is added depends on the specific technique used. Each one has its own characteristics, advantages and limitations. Extrusion processes are the most common ones among AM. To form final pieces with these processes, the material is forced through a nozzle and deposited creating a three dimensional matrix. The need of a post treatment also depends on the technique. Nevertheless, all AM processes produce final or near-final pieces.

This work aims to study the possibility of formulating sodium borosilicate glass (NBS) inks for Direct Ink Writing (DIW), an extrusion based AM technique. DIW ceramic inks are highly viscous solutions with specific rheological properties that let them retain its shape after being extruded. These inks are commonly a mixture of ceramic powders and a rheological agent, however, it is also possible to mix ceramic precursors with rheological agents to formulate them.

Specifically in the synthesis of silica and silica derivate glasses, the ceramic powder method is the most utilized. In contrast, little information can be found for the ceramic precursors approach. Therefore, a first approach to produce NBS glass from precursors has been studied.

Sol-gel method was used as the route to produce NBS glass from precursors. Addition of a poloxamer (Pluronic-F127) was explored to achieve the rheological behaviour desired and different inks where formulated. The rheological properties of the inks formulated

were characterized, being the most suitable ones printed and sintered to verify the feasibility of the process developed. Finally, a series of characterization techniques were proposed to fully determine the properties of the material synthesized.

Sol-gel method is suitable to form NBS glass from precursors and the optimizations explored gave positive results. Pluronic-F127 as rheological agent in combination with the NBS glass solution behaves as a pseudoplastic non-Newtonian fluid. The highest loaded printable ink is the formulation with a content of 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume. Higher concentrations of NBS-12 cannot retain the given shape after printing.

Altogether, it is possible to produce printable NBS glass inks as a proof of concept. The sintered samples are unable to retain their given shape and the final appearance is not the expected one, however, the process developed does yield a final NBS glass piece.

### 3. RESUMEN

La manufacturación aditiva (AM), hace referencia a una serie de técnicas en las cuales, en contraste con las técnicas de manufacturación tradicional, las piezas finales se consiguen por adición de material en vez de substrarlo. Estas tecnologías se han estado desarrollando por más de 24 años y también se hace referencia a ellas como Prototipado Rápido, Fabricación de forma Libre, Manufacturación en capas, impresión 3D entre otros, siendo todos ellos sinónimos. Con el uso de estas técnicas, Se pueden producir formas complejas con prácticamente cualquier material, permitiendo aplicaciones virtualmente infinitas para las técnicas de AM.

La forma en como el material se adiciona depende de la técnica específica utilizada. Cada una tiene sus propias características, ventajas y limitaciones. Los procesos de extrusión son los más comunes entre AM. Para formar piezas finales con estos procesos, el material es forzado a través de una boquilla y depositado creando una matriz tridimensional. La necesidad de un tratamiento posterior también depende de la técnica. Sin embargo, todos los procesos de AM producen formas finales o casi finales.

El objetivo de este trabajo es estudiar la posibilidad de formular tintas de vidrio de borosilicato de sodio (NBS) para Impresión Directa de Tinta (DIW), una técnica de AM basada en extrusión. Las tintas cerámicas de DIW son soluciones altamente viscosas con propiedades reológicas específicas que les permiten retener su forma después de ser extruidas. Estas tintas son comúnmente una mezcla de polvos cerámicos y un agente reológico, sin embargo, también es posible mezclar precursores cerámicos con agentes reológicos para formularlas.

Específicamente en la síntesis de vidrios de silicio y vidrios derivados del silicio, el método de polvo cerámico es el más utilizado. En contraste, poca informas puede ser encontrada de la aproximación utilizando precursores cerámicos. Por lo tanto, se ha estudiado un primer enfoque para producir vidrio NBS a partir de precursores.

Se utilizó el método sol-gel como la ruta para producir vidrio NBS a partir de precursores. Se exploró la adición de un poloxámero (Pluronic-F127) para conseguir el comportamiento reológico deseado y diferentes tintas fueron formuladas. Las

propiedades reológicas de las tintas fueron caracterizadas siendo las más aptas impresas y sinterizadas para verificar la viabilidad del proceso desarrollado. Finalmente, se propuso una serie de técnicas para determinar por completo las propiedades del material sintetizado.

Se determinó que el método sol-gel es adecuado para formar vidrio NBS a partir de precursores y las optimizaciones exploradas dieron resultados positivos. El Pluronic-F127 como agente reológico, en combinación con la solución de vidrio NBS se comporta como un fluido no newtoniano pseudoplástico. La tinta imprimible de más cargada fue la formulación con un contenido de 75% PLU-F127 33% (w/w) + 25% NBS-12 en volumen. Mayores concentraciones de NBS-12 no pueden retener la forma dada después de ser impresas.

En total, es posible producir tintas de vidrio NBS imprimibles como prueba de concepto. Las muestras sinterizadas no pueden mantener su forma dada y la apariencia final no es la esperada, sin embargo, el proceso desarrollado produce una pieza final de vidrio NBS.

## **4. INTRODUCTION**

The concept of Additive Manufacturing (AM) refers to a series of techniques in which the final forms are creating by adding material instead of subtracting it. Thus, in order to produce a piece, a material is stacked in layers until it reaches the final product. These technologies have been developing for more than 25 years and they are also referred to as Rapid Prototyping, Freeform Fabrication, Layered Manufacturing, 3D Printing and others, being all synonyms [1]. Even though most of the techniques where already known by the 90's decade, many were in pre-commercial states and were little more than experimental concepts [2]. Nowadays, the fields of application of AM are virtually infinite. Manufacturing of scaffolds for bio-medical applications, intricate parts for automotive industries, prototypes in aero-space companies are just a few examples of how broad AM can be exploited [3].

The principle of AM is also quite unique. The process begins with an idea which is then transferred to a Computer-Aided Design (CAD) model. Using CAD, makes possible to have a real-time overview of the model and to make fine adjustments until reaching the intended final form. Once the requirements are met, it is then converted to a special format and programmed into the machinery. The piece is produced autonomously and the end product is a fully functional piece with geometries that can be very intricate, complex and even unobtainable by other manufacturing processes with little to none post-processing [2-3].

The different processes in which AM has branched, differ in the method used to create and deposit the layers. How processes are classified depend on the author consulted. Here, they can be found by the mechanism for the continuous layer deposition and the bulk material used: solid, powder, liquid or gas (Figure 1) [1-2]. The earlier processes were limited to only polymeric materials and the final pieces did not meet the requirements to be engineering materials [1]. Further comprehension on materials science and

engineering have made possible to create functional pieces made out of any material family through AM.

Major family processes can be sorted as [4]:

- Laser-based: use interactions between the laser light and phase changes in the material to create each individual layer of the desired model.
- Extrusion processes: a material, of proper rheology, is forced through a nozzle creating a matrix. The process repeats itself adding layer upon layer.
- Material jetting processes: material is jetted, through a nozzle, on a building surface. It solidifies and the piece is build layer by layer.
- Adhesive processes: materials are fed as thin layers which stack on top of the previous one. The layers are glued together with aid of heat and pressure.







Additive Manufacturing (AM) Processes												
Process	Laser Based AM Processes					Extrusion Thermal	Material Jetting	Material Adhesion	Electron Beam			
	Laser Melting		Laser Polymerization									
Process Schematic												
Name	Material	SLS	DMD	SLA		FDM	3DP	LOM	EBM			
		SLM	LENS	SGC		Robocasting	IJP	SFP				
		DMLS	SLC	LTP			MJM					
			LPD	BIS			BPM					
				HIS			Thermojet					
Bulk Material Type		Powder	Liquid	Solid								

Figure 1. Categorization of additive manufacturing processes [4].

Each of this processes have specific characteristics and their own limitations. However, in general, AM offers a copious amount of advantages. The most mentioned one is the enormous time and cost saving in prototyping. Since CAD models are easy to review and modify, errors can be detected and corrected, reducing significantly the number of iterations in the design and prototyping process. As the approach is of an additive nature in contrast to the subtractive, in conventional manufacturing, low waste is produced and sometimes it can be recovered to be reused. The ease by which waste can



be recovered and reused depends on the AM technique. In most of the cases, the parts produced require little extra tooling or auxiliary resources, making AM also resource efficient. Flexibility of the process is also one important feature of AM, batch size is easily adaptable with possibilities of customization according to the necessities. The complexity that can be reach with AM processes grant the ability to create functionality optimizations in the parts that could be impossible by other methods. All of these facts highlight the feasibility for innovation of AM [1,3,5-6].

However, AM also has important drawbacks. The part size is constraint by the machinery dimensions. Although, many AM technologies can achieve great dimensional tolerances with smooth surfaces, others leave rough surfaces which may cause loses in mechanical properties and an unfinished look. Often, the time required to produce one single part, depending on its complexity, can be very high. This implies that to produce bigger batches either long waiting times are required or more machines if extended times are not possible [3]. Finally, there are many materials which present complex challenges to manufacture through AM with the current technologies.

The aim of this work is to explore Direct Ink Writing (DIW), an extrusion based AM process, also known as robocasting, robotic material extrusion, direct-write assembly or 3D-plotting [7]. DIW operates by forcing a paste through a nozzle in order to create the layers for a desired architecture. The pastes are referred to as “inks” due to the simile of the process with traditional printers [7-8]. In general, extrusion based processes require temperature controlled nozzles or deposition beds. Fused Deposition Modeling (FDM) requires heated nozzles in order to extrude polymeric filaments and Low-temperature Deposition Manufacturing (LDM) uses low temperature deposition beds to retain the part shape by freezing the solvents [7]. As opposite to these techniques, DIW does not require thermal control and can achieve high resolution using small diameter nozzles. Ink formulation is a critical step for DIW Process. To be printed, inks must have specific rheological behaviour, high storage modulus and excellent shape retention capacity. These characteristics make DIW a flexible AM process and, at the same time, a complex one [7–9].

Typically, DIW inks are solutions with a non-Newtonian, pseudoplastic behaviour. In terms of rheology, it means the ink's viscosity must decrease with an increment of the

applied shear rate which is related to the applied stress onto the ink. Inks must be able to flow through the nozzle then set immediately after to retain the given shape. Inks are extremely sensitive, meaning every component play a key role since they determine how “fluid” inks can be and whether if they are suitable for printing or not. These parameter are not fix, they are tailored for each application and printer [8-9]. DIW, as a flexible process, allows to produce inks with relative ease from many different materials and finished parts often possess good mechanical properties [10].

To produce ceramic inks, two approaches are used in DIW processes. The first one is based on ceramic powder suspensions. Generally, the suspensions are aqueous or organic based and it depends on the nature of the ceramic powders, the rheological agents used to achieve the desired viscosity and the final applications for the inks. The other approach utilizes ceramic precursors which react when sintered to form the proper ceramics. To make these inks, ceramic precursors are mixed together with a rheological agent to give them the proper behaviour. If required, the solutions could also be loaded with ceramic powder to achieve higher densification [9,11].

One particular topic of increasing interest is the synthesis of silica and silica derivate glasses through DIW AM processes. As opposite to traditional melt and quenching techniques, AM allows to produce complex, functionalized shapes. Silica glasses and silica derived glass have numerous applications in fields such as medicine, optics and energy production [12]. To produce these inks, the general path is to create a solution of ceramic powder as mentioned before. These ceramic powders can usually be obtain commercially, however, they can also be synthesized by different methods for those applications which required more specific and complex compositions [12–14].

There are many reports of ceramic inks for different AM processes where the final pieces are obtained from ceramic precursors, mixed with a rheological agent [9,15–17]. However, little information could be found of the same principle applied to silica glasses nor silica derived glasses. Producing final pieces from precursors is an alternative path for ink formulations that allows the process to be less time consuming and saves resources by skipping the powder production section (Figure 2).

This study proposes a first approach into achieving printable sodium borosilicate (NBS) glass inks. It aims to find a suitable route which allows to form NBS glass from

precursors. Once the route is found, a characterization and tailoring of its rheological behaviour will be performed in order to make it suitable for printing through DIW technique. Finally, sintering tests will be carried to verify the feasibility of the process developed.

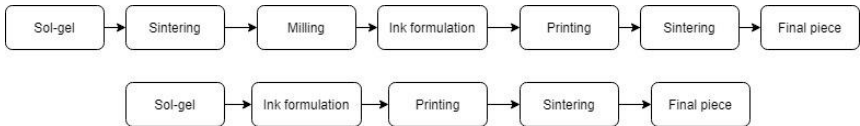


Figure 2. Difference between traditional path and precursor's path to produce a final piece starting from sol-gel method.

## 4.1. OBJECTIVES

The main objective is achieving a formulation of a Sodium Borosilicate glass ink, from precursors, suitable for Direct Ink Writing technique. In order to do so, proper reagents must be mixed together following a route to establish a method able to synthesize the sodium borosilicate glass from precursors.

Given the specific nature of inks for DIW technique, rheological behaviour must be characterized and tailored to obtain a pseudoplastic behaviour and establishing the maximum load of glass-forming species allowed by the system. Once these specifications are met, several ink formulations will be proposed.

The inks formulated will be characterized and, the ones presenting the best combination of the parameters described, will be printed. Finally, a sintering process will be carried out to verify the feasibility of the process developed.

## 5. INK FORMULATION

To formulate a printable ink from precursors, a number of parameters must be met. A route to combine the precursors into the desired material (sodium borosilicate glass) must be found, the rheological behaviour must be adequate and the ink must be as loaded with the precursors as possible. Achieving these parameters represent a challenge. Precursors are usually highly unstable and tend to react with the media they are in. Often, rheology needs to be adjusted and the amount of material that can be loaded into the inks may not be as high as wanted.

In this section, a route to form NBS glass is proposed, developed and explained. Whilst the route proved to be successful, the rheological behaviour was not the adequate. Pluronic-F127 (PLUF-127) was then proposed as a rheological agent to be able to formulate inks. Ethanol (EtOH) was used as solvent for the NBS glass route proposed. When EtOH is mixed with PLU-F127, in high concentrations, it becomes unable to undergo a sol-gel transitions. The limit concentrations to avoid this phenomenon were determined.

Using the information gathered, the NBS solution was mixed with PLU-F127, different inks were formulated and their rheological behaviour was characterized and presented.

### 5.1 SOL-GEL METHOD.

Sol-gel method has been selected as the route to synthesize sodium borosilicate (NBS) glass from precursors. It consists on creating a homogeneous disperse solution called “sol” which then forms a rigid “gel” through a destabilization process that induces this phase change [18]. Historically, silica gels have been of particular interest since mid-1800's due to its ability to form glass-like materials [19]. To form gels in the silicate glass systems two mechanisms can be used. The first mechanism is based in the gelation of silica hydrosol and the second is based in polymerization reaction of alkoxisilanes [18].

According to the consulted authors, the mechanism used to produce NBS glass is based in the polymerization of alkoxisilanes [20–22]. In general, the process involves the catalysed reaction of an alkoxisilane, typically tetraethoxisilane (TEOS), with water in a common solvent. The TEOS is hydrolysed and forms silanol monomers which condense

forming a cross-linked network [23]. Concentration of the alkoxisilanes, pH of the medium, temperature, nature of the solvent and amount of water are key factors, they define the kinetics of the reaction which determine the properties of the final gel formed [18,23].

### 5.1.1. Experimental procedure

A modified process from Osaka, Mukherjee and Copenhaver [18,20-21] was used to produce NBS glass sol-gels of composition: 80%SiO<sub>2</sub> · 15% B<sub>2</sub>O<sub>3</sub> · 5% Na<sub>2</sub>O (wt%). TEOS and sodium ethoxide (NaOEt) were used as the source of SiO<sub>2</sub>, and Na<sub>2</sub>O respectively. For the selection of the source of boron oxide (B<sub>2</sub>O<sub>3</sub>), the hydrolysis mechanism of trimethyl borate (TMB) was studied. TMB is an organoboron compound, when it reacts with water forms ethanol (EtOH) and boric acid (H<sub>3</sub>BO<sub>3</sub>). Then, boric acid can be oxidised by heating it over 300°C to form boron oxide (Figure 3). Therefore, for ease of access and compound stability, boric acid was selected as the source of B<sub>2</sub>O<sub>3</sub>.

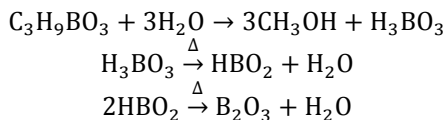


Figure 3. TMB reaction mechanisms to form boron oxide.

The amount of water must be precisely monitored because reagents undergo hydrolysis and each of the reactions need a specific stoichiometric quantity. The total amount needed can be calculated using the Equation 1.

$$w(\text{H}_2\text{O}) = 2(\text{TEOS}) + \frac{1}{2}(\text{NaOEt}) \text{ (mol)} \quad \text{(Equation 1)}$$

To verify the reagents worked the intended way, preliminary tests were carried. To produce the NBS sol-gel, a solution of TEOS (purchased from Sigma-Aldrich), Absolute EtOH, water and HCl was prepared, pH was measured giving a pH of 4 and the solution was stirred during one hour at 40°C. Molar ratios used were 1:100 for HCl to TEOS and 3:1 for EtOH to TEOS. The amount of water was determined by the stoichiometry of the reactions and it is given by the Equation 1. H<sub>3</sub>BO<sub>3</sub> in a concentration of 1.5 M was added next, pH was measured again with no changes to report and the solution was let to stir

for another hour at 40 °C. Finally, NaOEt 2.06 M, synthesized in the laboratory [24], was incorporated to the solution. Upon addition, a rise in the pH was measured, it rose from a pH of 4 to a pH of 6. As it was mentioned before, the morphology and final properties of the gels are pH dependant. In acid solutions, the hydrolysis process is predominant over the polycondensation, while the opposite occurs in basic solutions [18,25]. In order to keep a balance between the competing mechanisms and avoiding premature gel formation, the solution was acidified to a pH of 3 using concentrated HCl (aprox. 1 ml). The sudden change in pH due to the addition of concentrated HCl caused the solution to form a white precipitate.

Since the precipitation was caused by the extra addition of the HCl, the same route was tried again. The proportions and procedures were kept. Once the NaOEt was added, pH was measured giving a pH of 6 and the solution was let to stir for another hour at 40 °C. The result was a clear, homogeneous solution. In order to verify the gelling time, a qualitative test was made. Gelling time is defined here as the time needed for the solution to convert into a non-flowing, self-sustaining gel. The test consisted in pouring 5 mm of the solution into a glass vial, seal it tightly and shake it every minute until the gel point is reached. After 25 minutes a drastic increase in the viscosity was observed, however, it still was able to flow. At 27 minutes the gel reached its gelling time, viscosity was high enough to self-sustain and not flow. The test continued further until the total gelling of the solution at 32 minutes. The route, called sodium borosilicate 4 (NBS-4), is presented in Figure 4.

Once a working route was found (NBS-4), further optimization was carried out. Gelling time was too short and the gel produced was not adequate to be printed. In order to extend it, two strategies were explored: an increase in the amount of water by mol of TEOS and temperature variations. As mentioned before, both parameters have strong influence in the sol-gel method and their effects were determined. The results can be summarized as follows: Doubling the amount of water by mol of TEOS caused the formation of precipitates upon addition. Either increasing the temperature to 60 °C or decreasing it to room temperature caused the gel to form prematurely.

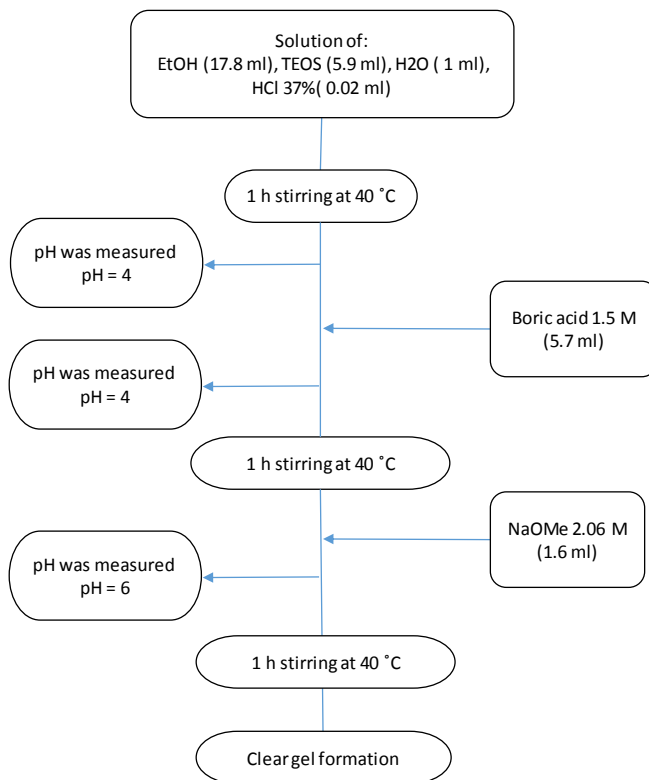


Figure 4. Flux diagram of NBS-4 route

The NBS sol-gel route selected is time consuming. A variation in the order of the reagents was made to minimize the mixing time. Instead of adding the boric acid in a second stage, it was incorporated in the initial solution. Thus, the procedure was modified as follows: a solution of EtOH, TEOS, water, hydrochloric acid and boric acid was prepared, the solution was let to stir one hour at 40 °C. Then, the NaOEt 2.06 M was added and let to stir for another hour at 40 °C as. After letting it gel, the result was a clear and homogeneous gel which proved the new route, sodium borosilicate 11 (NBS-11), to be viable.

Nevertheless, the gelling time was still a major concern. It is not constant and fast gelling impedes the solution to be prepared in advance and stored. In this regard a further study of the mechanisms was carried out to give with a workable solution. The sol-gel

reaction, as mentioned before, consists in two parts. The first part is a hydrolysis reaction, where the TEOS forms monomers and, in the second part, these monomers condense forming the gel. If no monomers are formed, no polycondensation can occur, therefore, the proposed solution was to recreate the working route (NBS-11) in absence of water.

Without the water, the result was a clear and homogeneous solution. Another Qualitative test was carried out to verify and compare gelling times. This time, 5mm of solution NBS-11-dry were poured into six different vials. To three of them, the stoichiometry water was added. For each set of three vials, two of them were closed tightly and, in the last one, the lid was let loose. Of the sealed vials, one was stored in the fridge and the other one let at room temperature with the loosed lid vial. None of the sealed vials without water gelled. The loosed lid vial absorbed water from the atmosphere and did gel. In contrast, all of the vials with the added water gelled completely. The use of this variation of the selected route, makes possible to prepare the solution in advance and store it for later use.

Table 1. Summary table showing gelling test

Composition	Conditions	Gelling
NBS-11-dry	Sealed + room temperature	NO
	Sealed + refrigeration	NO
	Not sealed + room temperature	YES
NBS-11-dry + water	Sealed + room temperature	YES
	Sealed + refrigeration	YES
	Not sealed + room temperature	YES

Finally, the last optimization made, was to reduce the amount of solvent from the original molar ratio used of 3:1 of EtOH to TEOS to a ratio of 1:3 EtOH to TEOS. The reason behind this optimization is to increase the concentration of glass forming species to reduce the amount of ink needed to produce a final piece. While the original ratio worked properly, it meant that for every gram of NBS glass 16.1 ml of solution must be prepared which implied that to produce, even small pieces, great amount of solution was required and, furthermore, a great amount of ink. Additionally, given the small amount of



solvent used and the tendency of the solution to absorb atmospheric water, another modification was introduced to the route. Instead of mixing the reagent open to the atmosphere, the mixing beaker was covered with plastic film to prevent solvent evaporation and the aforementioned atmospheric water absorption.

The final solution turned to be clear and homogeneous with no sign of precipitates. Several visual inspections were made during the course of a week to check the stability of the solution and gelling. No changes were appreciated during this period of time, making this route, sodium borosilicate 12 (NBS-12), the most efficient among the ones studied (Figure 5).

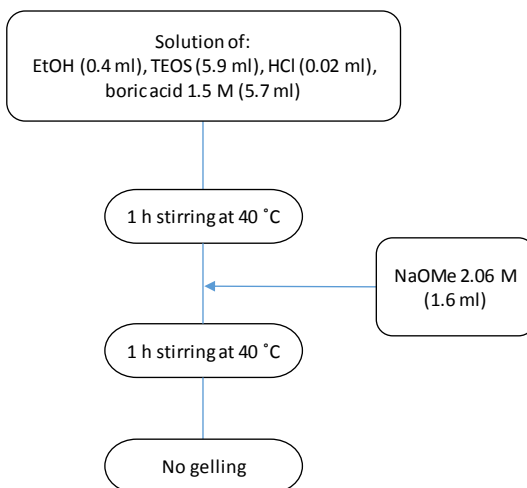


Figure 5. Flux diagram of NBS-12 route

## 5.2. RHEOLOGICAL CHARACTERIZATION

Inks for DIW, an extrusion based AM technique, requires specific rheological behaviour to be able to print. They must be able to flow through a nozzle while a force is applied to them and immediately settle after to avoid sagging and general deformation. To achieve this, non-Newtonian pseudoplastic fluids are needed. This kind of fluids, also known as shear thinning, are characterized for being non-time dependant and for decreasing its viscosity with an increase of the shear stress or the shear rate applied to

them [26]. While they are among the most used non-Newtonian fluids in the industry, achieving this behaviour requires a precise control in all the parameters of the process [27]. As it is known, rheological properties are heavily dependent on temperature, shear stress, shear rate and highly susceptible to atmospheric conditions as barometric pressure and relative humidity [26].

In this section, the rheological properties of the NBS-12 gel were studied. PLU-F127 was used as rheological agent to achieve the desired behaviour. PLU-F127 with EtOH was optimized to determine the limits in which they could be mixed together while maintaining a pseudoplastic behaviour and, finally, with the results obtained, several ink formulations of PLU-F127 + NBS12, in different concentrations by volume, were proposed and characterized.

### 5.2.1. Experimental procedure

Firstly, to verify the general behaviour of the NBS-12, a qualitative test was performed. A portion of the stored NBS-12 solution was poured into a beaker and the corresponding stoichiometric water was added. The solution was stirred vigorously to fully mix the water with the solution and let to gel. Once the gel was fully formed, it was stirred again with a spatula. Instead of flowing, like the desired behaviour, the gel shattered and crumbled. By itself, even though the gel is self-sustaining, could not be printed.

To produce printable inks, the approach taken was to mix the NBS-12 solution with a rheological agent of the desired behaviour. For this matter, poloxamer-407, also known as Pluronic-F127 (PLU-F127) was selected. Poloxamers are copolymers formed by three blocks: a centre block of polypropylene oxide (PPO) with hydrophobic characteristics and two outer blocks of polyethylene oxide (PEO) with hydrophilic characteristics. PLU-F127 was selected due to its thermo-reversible gelation properties. It is capable to undergo a thermo-sensible transformation from a liquid-like behaviour to a gel-like behaviour, in concentrated aqueous solutions, which happens to behave as a pseudoplastic fluid. The temperature, at which this change is produced, is called sol-gel transition temperature [28].

The mechanism that rules the transformation involves the hydrophobic and hydrophilic nature of the blocks and it can be divided into two steps. The first step occurs

upon reaching the sol-gel transition temperature, at this step, the hydrogen bonds between water and hydrophilic chains, which separate the hydrophobic portions of the poloxamer, break and hydrophobic bonds are formed in order to avoid a decrease in the entropy of the system. This causes the poloxamer to form spherical micelles consisting in an outer shell of hydrated PEO and a core of hydrophobic PPO [28-29]. The second step occurs when the temperature is increased even more and the micelles pack themselves forming a gel.

Sol-gel transition temperature is rather a characteristic of the system than the poloxamer itself. The concentration of the poloxamer, fillers, pH and addition of solvents modify this temperature. It has been reported that an increase in the concentration of the poloxamer reduces the sol-gel transition temperature, while the addition of solvents as EtOH also reduces it until a certain fraction (measured in volume) and then increases until it can no longer undergo sol-gel transition. It is believed this phenomenon may occur due to a prevention of hydrophobic interactions and micelle formation in presence of EtOH [30-31].

The ideal ink must be as loaded as the system allows it. This means that to produce an adequate ink, there should be possible to mix the highest percentage possible of NBS-12 solution into the PLU-F127. Given the fact that the effects of increasing concentration and adding EtOH as a solvent have opposite effects, the highest workable concentration of PLU-F127 in aqueous solution was explored. Concentrations around 20% (w/w) to 30% (w/w) has been studied, and reported a sol-gel transition temperature oscillating between 4 °C and 5 °C. Concentrations above 35% (w/w) require temporary freezing of the solution to allow the poloxamer to properly dissolve, furthermore, Sol-gel transition temperature decreases to around 0 °C making it complicated to mix with the NBS-12 solution to produce a printable ink [30,32]. Therefore, a concentration of 33% (w/w) was proposed and studied.

To create the solution at a 33% (w/w) concentration, the proper amount of PLU-F127 (purchased from Sigma-Aldrich) was weighed and slowly added to the corresponding amount of deionized water, previously cooled in an ice bath to facilitate mixing. The solution was stirred until reaching a homogeneous solution and stored in the fridge during a period of two days to allow the foam formed in the process to banish.

Even though NBS-12 solution contains EtOH as the solvent, it also contains a mixture of other substances. However, pure EtOH will be used as a starting point to determine the maximum allowed percentage of NBS-12 that can be mixed with PLU-F127 while keeping the desired rheological properties. In this regard, different solutions were prepared by adding the corresponding amount of EtOH to the PLU-127 solution to form concentrations from 0% to 25% of EtOH to PLU-F127 selected solution (v/v).

### 5.2.2. Rheological characterization

The characterization was made by rheometer, model Discovery HR-2 and a 40 mm, 1.019° cone-plate, Peltier plate Steel geometry. Two different tests were carried out:

- A temperature sweep performed by steps from 4 °C to 40 °C with increments of 2 °C, at constant shear rate of 1 s<sup>-1</sup> to determine sol-gel transition temperature and maximum viscosity.
- An oscillatory stress sweep from 1 Pa to 1000 Pa at a constant frequency of 1 Hz and a constant temperature (depending on the sample tested) to determine storage modulus ( $G'$ ) and loss modulus ( $G''$ )

#### 5.2.2.1 Temperature sweep

Temperature sweeps are a common test performed to determine the dependence of the viscosity with the temperature. Often, it can also be used to determine critical temperatures that induce transformations in the materials as it is the case of poloxamers [33].

Every single one of the samples was tested as described in the section 5.2.2. The results can be observed in the Figure 6. The sol-gel transition temperature decreases with an increase with the content, by volume, of EtOH from 0% (v/v) up to 15% (v/v). After this point, however, the sol-gel transition temperature increases. This behaviour corresponds with the reported data consulted [28]. Even though a content of 20% (v/v) of EtOH presents low viscosity, in relation with lower contents in EtOH, it forms a proper gel with a pseudoplastic fluid behaviour. The sample with a content of 25% (v/v) of EtOH does not gel properly, thus, formulations with a higher content in EtOH are discarded.

According to these results, the highest achievable concentration of EtOH (v/v) for a solution of PLU-F127 at 33% (w/w), that does not lose the desired properties, corresponds to 20%. This will be the starting point for further measurements and ink formulations.

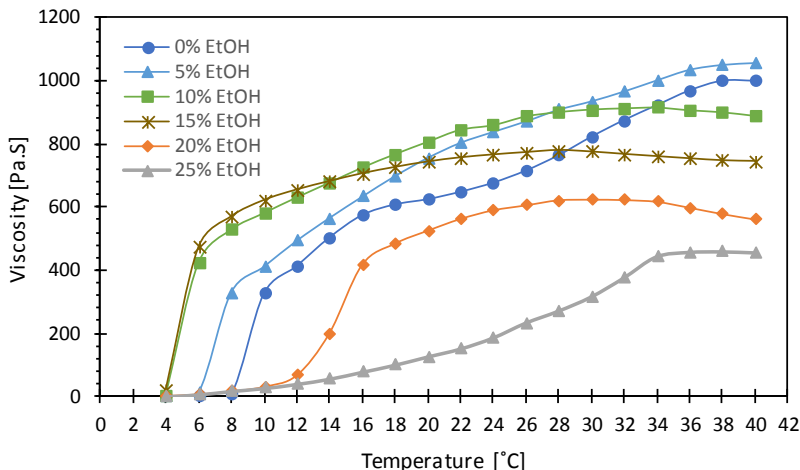


Figure 6. Viscosity as a function of temperature for different concentrations of EtOH (v/v)

#### 5.2.2.2 Oscillatory stress sweep

Most of materials have mixed characteristics between an elastic and viscous behaviour. Oscillatory measurements allow to characterize and derive many properties of the material as the molecular weight, structural information, crosslinking, particle size and shape, among others. These measurements are carried out by inducing an oscillating stress or strain and measuring the response of the material through a detector [33].

Oscillatory measurements can be performed as a function of any of the rheological variables (temperature, stress or strain amplitude, frequency or time). The intention of these tests is to measure the storage and loss modulus as a function of stress or frequency amplitude. These parameters determine whether the elastic or viscous behaviour is dominant. The storage modulus indicates how much energy is stored in the elastic structure of a material which correlates with how much structure is in a material. In contrast, the loss modulus represents the amount of energy dissipated in the sample. Dominant behaviour of materials also depends on the frequency. High frequencies tend to shift the material's behaviour towards predominant viscous. When oscillatory stress

measurements are performed, low frequencies are recommended to avoid behaviour shifts induced by the frequency [26,33].

Only the two most concentrated samples in EtOH, 20% (v/v) and 25% (v/v) were tested. For each sample, two different temperatures were studied, one below the sol-gel transition temperature and one above, 2 °C and 20 °C correspondingly. The rest of the parameters were used as described in section 5.2.2. The results, as seen in the Figure 7, show an interesting behaviour. Independently of the temperature, the storage modulus remains above the loss modulus for both samples. This fact means that more energy is stored than lost in the material. Which implies that even in liquid-like state, there is enough elastic structure to store the energy applied to the material. Finally, even though, the material may not have the proper viscosity at low temperatures to be printed, its dominant behaviour is of an elastic material.

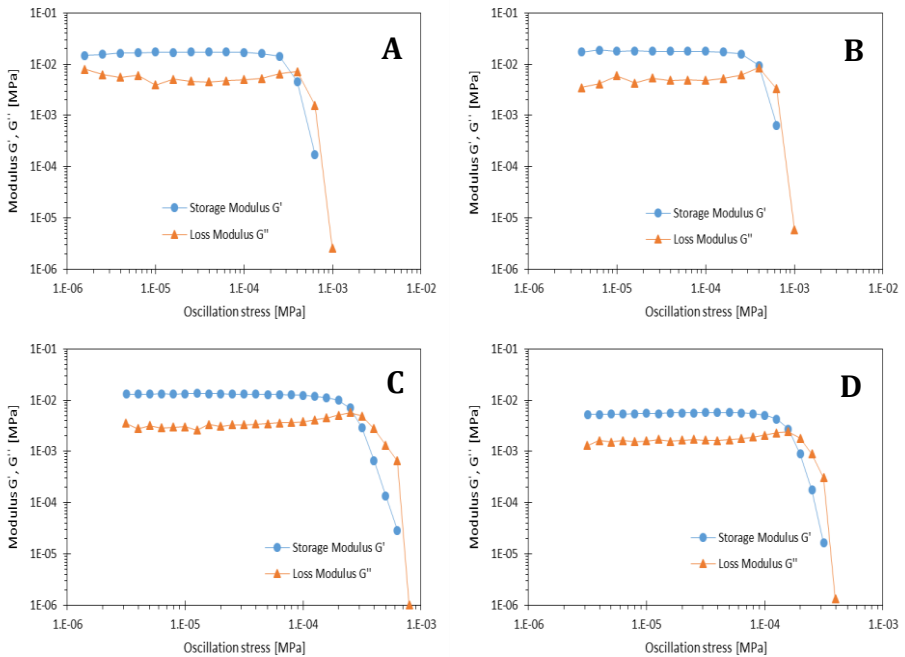


Figure 7. Measured modulus as a function of oscillation stress. Up: 20% EtOH (v/v), 2 °C (A) and 20 °C (B). Low: 25 % EtOH (v/v), 2 °C (C) and 20 °C (D).

### 5.3 INK FORMULATION

Based on the information gathered in the tests, the proposed ink formulation is of an 80% PLU-F127 33% (w/w) + 20% NBS-12 by volume. Furthermore, reiterating the fact NBS-12 solution not only contains EtOH and foreseen possible interaction between PLU-F127 and NBS-12 solution, two more inks with higher concentration of NBS-12 solution (v/v), were proposed. The inks are summarised in the Table 2.

Table 2. Summary of inks formulated

N°	Ink composition
1	80% PLU-F127 33% (w/w) + 20% NBS-12 by volume
2	75% PLU-F127 33% (w/w) + 25% NBS-12 by volume
3	70% PLU-F127 33% (w/w) + 30% NBS-12 by volume

#### 5.3.1. Experimental procedure

PLU-F127 33% (w/w) solution was cooled in an ice bath to liquefy it. NBS-12 solution was also cooled to avoid instantaneous localized gelling of the PLU-F127 solution. Once both were at the adequate temperature, the NBS-12 solution was poured into the PLU-F127 solution in the corresponding amounts for the desired formulations. The mixture was taken to a vacuum planetary mixer and was agitated vigorously for 50 seconds. A visual inspection was made to assure all the components were mixed properly. Whereas the mixture turned to be homogeneous with no traces of phase separation, it is worth to notice that a slight change was observed, the solution went from transparent to slightly white and translucent. This may be due a reaction between the NBS-12 solution and the water contained in the PLU-F127 solution.

After mixing, the inks were transferred to printing syringes and stored at room temperature to avoid phase separation induced by liquefying of the PLU-F127 solution.

### 5.3.2. Ink rheological characterization

Rheological behaviour, as mentioned before, is critical for a successful printing, therefore, each formulation was characterized. The characterization was made by the same equipment described in section 5.2.2.

- A shear rate sweep from  $1\text{ s}^{-1}$  to  $1000\text{ s}^{-1}$  at a constant temperature of  $20\text{ }^{\circ}\text{C}$  to verify pseudoplastic behaviour.
- A temperature sweep performed by steps from  $4\text{ }^{\circ}\text{C}$  to  $40\text{ }^{\circ}\text{C}$  with increments of  $2\text{ }^{\circ}\text{C}$ , at constant shear rate of  $1\text{ s}^{-1}$  to determine sol-gel transition temperature and maximum viscosity and to compare with the previous solutions of PLU-F127 and EtOH.

#### 5.3.2.1 Shear rate sweep

The three formulations were tested and the results are plotted in the Figure 8. As it can be seen, with an increase in the shear rate the viscosity decreases, which corresponds with the pseudoplastic, desired, behaviour. It can also be seen that the highest viscosity corresponds to the 80% PLU-F127 33% (w/w) + 20% NBS-12 by volume formulation and the lowest corresponds to the 70% PLU-F127 33% (w/w) + 30% NBS-12 by volume formulation. This result was expected given the fact that, as it was proved, the addition of substances to PLU-F127, causes interference with micelles formation, impeding proper gelling.



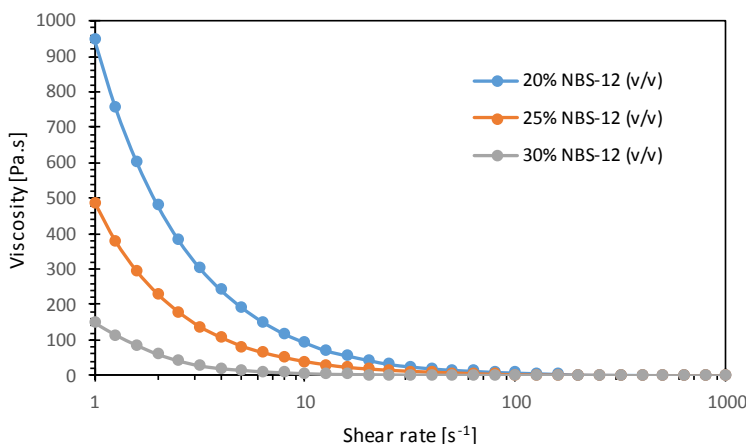


Figure 8. Viscosity as function of the shear rate for the three different inks formulated.

### 5.3.2.2 Temperature sweep

In addition to the three samples tested, presented in the Figure 9, the solution of PLU-F127 with a content of 20% (v/v) of EtOH (the reference selected as the starting point, without NBS-12 solution) was also represented to compare with the inks formulated. The ink formulation of 80% PLU-F127 33% (w/w) + 20% NBS-12 by volume presents the highest viscosity among the plotted samples. This result puts on evidence that NBS-12 containing solutions behave differently from those which only contain EtOH, possibly on account of different interactions between the PLU-F127 and the components in NBS-12 solution. The formulation of 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume has a slightly lower viscosity than the one containing 20% NBS-12, nevertheless, it is still enough to be self-sustaining making it suitable for printing. Finally, while the formulation containing 70% PLU-F127 33% (w/w) + 30% NBS-12 by volume does present an abrupt increase in the viscosity at 14 °C, implying a sol-gel transition, the maximum viscosity reached is not high enough and may no retain the given shape if printed. However, formulations containing 25% NBS-12 (v/v) and 30% NBS-12 (v/v) were selected for printing and sintering testing for having the highest, printable concentrations.

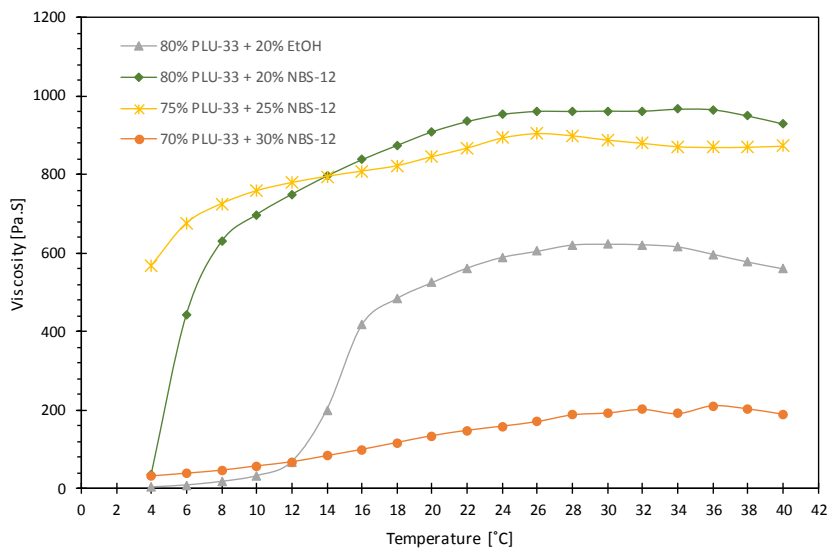


Figure 9. Viscosity as function of temperature for the different formulated inks compared with a solution of PLU-F127 with 20% EtOH (v/v)

## 6 SINTERING AND PRINTING

### 6.1 PRINTING TESTING

#### 6.1.1. Experimental procedure

The syringes containing the aforementioned formulations were taken to be printed in a CELLINK bio printer, model BIO X (Figure 10). Given the extremely sensitive nature of the ink's viscosity, the parameter of the printer needed to be tailored rather than set them as constants to achieve a continuous ink flow through the nozzle. Nevertheless, the tests were carried at ambient temperature and atmospheric pressure. For each ink, six samples were printed. The geometry selected was a cubic scaffold of dimensions 10x10x3 mm and an alternating grid as the infill pattern.

Sol-gel transition of the NBS-12 is a complex mechanism in which many parameters are involved. For each formulation, two of the six samples printed were taken to be sintered, two more were left to age in a stove at 37 °C and the two remaining were left to age at room temperature, covered in plastic film to promote a slow drying. In order to establish the best timing and conditions for sintering and how aging affects the final properties of the samples.

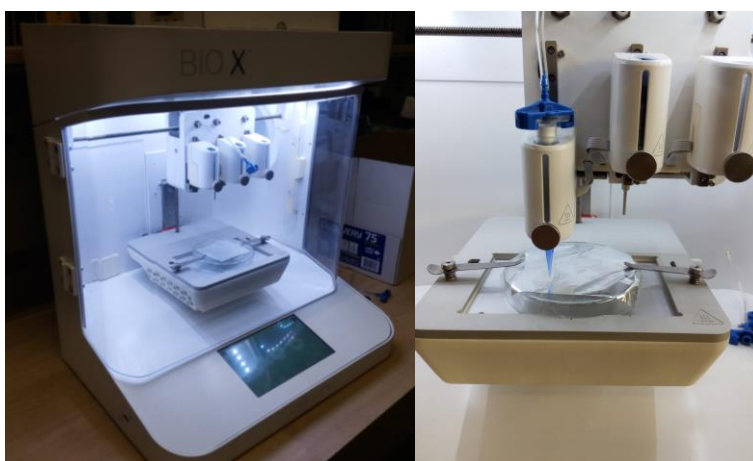


Figure 10. Bio printer model Bio X (left) and a detail of the printing bed (right)

### 6.1.2. Printing and aging results

Samples of formulation 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume were printed without problems. The parameters used were: printing velocities around 8 mm.s<sup>-1</sup> and 10 mm.s<sup>-1</sup>, nozzles of 100 µm and 200 µm and pressures between 100 kPa and 200 kPa. The structure formed was able to self-sustain itself and shape was properly retained. The stored samples left to age were inspected after three and five days. As it can be seen in the Figure 11, samples have suffered distortion as the result of the contraction forces caused by evaporation of the solvents. Distortion was significantly higher in samples aged in stove compared to the ones aged at room temperature. For the samples stored at room temperature, after three days, the approximate shrinkage calculated was (50±4)%. The samples stored in the stove presented an even higher approximate shrinkage of (63±11)%. The visual inspection after three days also revealed that, while the samples stored in the stove were totally dry, the samples stored at room temperature were still humid. No cracks could be appreciated in either of the samples.

The inspection carried after five days from printing, showed no appreciable difference and no further shrinkage compared to the third day inspection.

Samples of formulation 70% PLU-F127 33% (w/w) + 30% NBS-12 by volume were complicated to print, printer parameters were rectified several times during the process in order to achieve a continuous ink flow. Even more, the shape was not properly retained and, instead of a cube, the final shape consisted in a buckled-like cube shape. Nevertheless, once the ink settled, it no longer deformed and was able to self-sustain itself. The approximate shrinkage calculated, after three days, for the samples stored at room temperature was (46±1)% and for the samples stored in the stove was (59±4)%. This formulation presented a higher shrinkage in both of the aging conditions. Samples also suffered from deformation as can be seen in Figure 11 and one of the samples in the stoves presented a small crack. The other samples, beyond the deformation, did not showed signs of other appreciable defects.

Same as with the formulation 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume, no appreciable changes nor further shrinkage could be appreciated after five days.

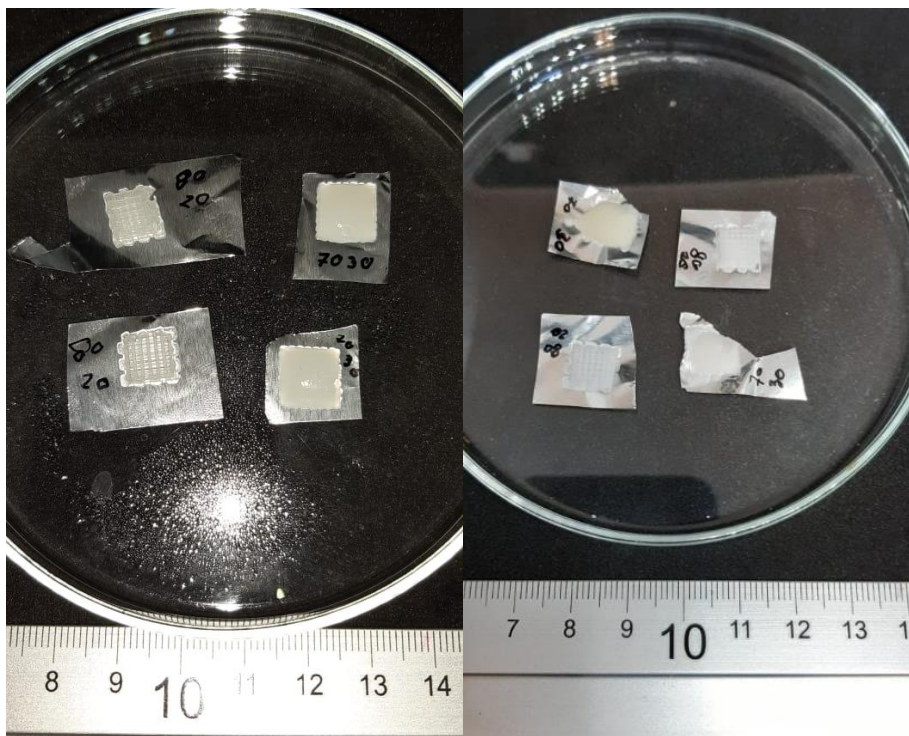


Figure 11. Aged samples, room temperature aged samples (left), stove aged samples (right)

## 6.2 SINTERING

Sintering stage is key in the process. It determines the final properties of the material and must be carried precisely to avoid thermal tensions which could break the samples. Even more, the formulated inks contain solvents (water and EtOH), organic matter and other volatile substances. If the thermal treatment is too aggressive, these volatile substances may induce internal forces which could also break the material. Therefore, the proposed thermal treatment must be performed by stages, allowing the different substances to leave the printed shapes at a slow pace and the final compounds to be formed.

The thermal treatment used is a modification of several thermal treatments consulted [18,21,34]. It consists in 7 steps in succession (Figure 12). Firstly, a slow heating is needed to assure all the piece is heated evenly, so the heating ramp must be low. Then,

a soaking time is mandatory to allow the water and EtOH to evaporate without creating strong tensions inside the material. The following ramps, while still must be low to guarantee an even heating, can be slightly higher given that the most volatile materials have already leaved the piece after the first soaking time. Finally two more soaking times are needed, the first one to combust the organic matter and the second one to fully sinter the piece. The different steps are listed next:

- Temperature ramp from room temperature to 150 °C at a rate of 0.5 °C/m.
- Hold stage at 150 °C for 5 hours
- Temperature ramp from 150 °C to 450 °C at a rate of 1 °C/m
- Hold stage at 450 °C for 2 hours
- Temperature ramp from 450 °C to 900 °C at a rate of 1 °C/m
- Hold stage at 900 °C for 2 hours.

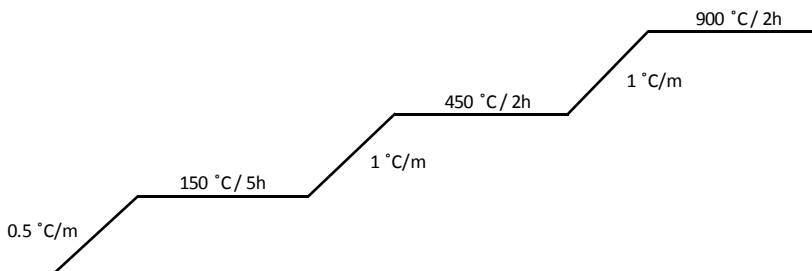


Figure 12. Visual representation of the thermal treatment proposed

### 6.2.1. Samples sintered after printing

The two samples sintered of formulations 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume and 70% PLU-F127 33% (w/w) + 30% NBS-12 by volume were printed directly on top of an alumina plate. After the thermal treatment, the plate was let to cool inside the furnace and, when retrieved, the sintered samples could be observed (Figure 13). This means it is actually possible to produce NBS glass, from precursors, trough DIW technique. None of the samples, however, retained the given shape after the sintering nor resulted in transparent glass. The shape loss may be an indicator of insufficient remaining material after all the volatiles are evaporated causing the piece to be unable to form a

continuous solid and crumbling. The whitish colour could be because of two reasons. On one hand it could mean the material did not fully sinter, causing, instead of a clear, transparent and monolithic glass, a conglomerate of small particles. On the other hand, it could be an indicator of a crystallization process during the sintering phase instead of the vitreous material expected.

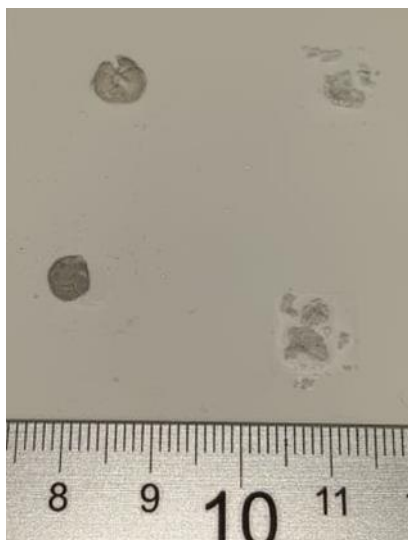


Figure 13. Samples after thermal treatment, left: 70% PLU-33% + 30% NBS-12, right: 75% PLU-33% + 25% NBS-12

When compared, the two formulations present a noticeable difference between them. The ink formulation with a content of 30% NBS-12 (v/v) retained better the original shape and remained less fragile than the one containing only 25% NBS-12 (v/v) which could be an indicator to confirm the aforementioned hypothesis referred to the shape loss.

### 6.2.2. three days aged samples

After three days aging, the samples, printed in aluminium foil, got stuck and it was not possible to separate them without breaking the pieces, therefore, they were sintered on top of the aluminium foil (Figure 14). After the thermal treatment, almost no sample remained from both pieces with a content of 25% NBS-12 (v/v). It is uncertain whether it was due to an unexpected reaction with the aluminium foil or to the aging process. In

contrast, the samples with a content of 30% NBS-12 (v/v), while stuck to the aluminium foil, did sinter. Although no cracks could be appreciated, the shape was not retained and did not turned transparent. The reasons are believed to be same as mentioned in section 6.2.1.

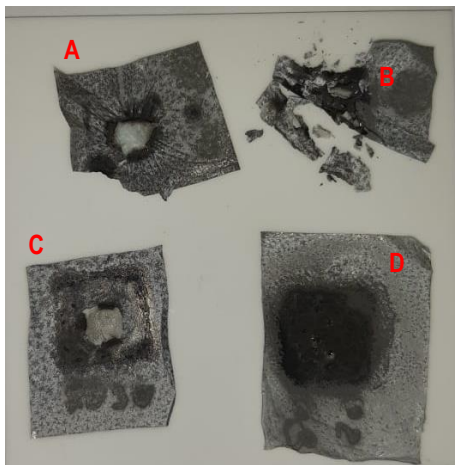


Figure 14. Sintered samples after 3 days of aging. (A) stove aged 30% NBS-12 (v/v), (B) stove aged 25% NBS-12 (v/v), (C) room temperature aged 30% NBS-12 (v/v), (D) room temperature aged 25% NBS-12 (v/v)

### 6.2.3. Five days aged samples

These samples were also printed on top of aluminium foil. In order to avoid the samples to get stuck again, they were separated. During this process, samples aged at room temperature shattered and were discarded. The stove aged samples did came apart and were sintered on top of an alumina plate using the same thermal treatment as all of the above.

This time, both samples sintered properly but none of the inks retained their original shape after sintering (Figure 15). The remaining sample with a content of 25% NBS-12 (v/v) formed a cracked film stuck to the alumina plate. It completely shattered, but the pieces had a glass-like look. The sample with a content of 30% NBS-12 (v/v) formed a bead with a greyish colour. This colour could be an indicator of some organic matter trapped inside the structure of the glass.



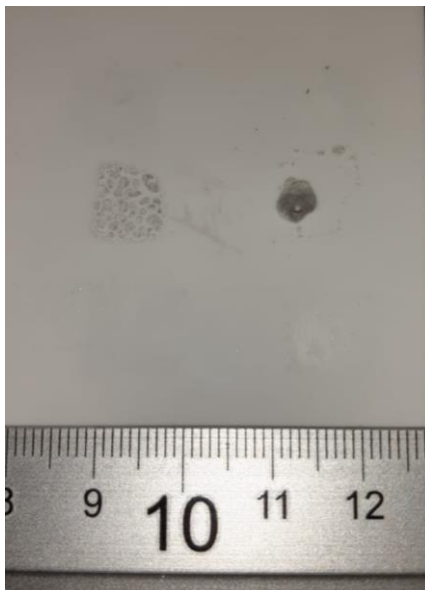


Figure 15. Five days stove aged and sintered samples. Left: 25% NBS-12 (v/v) formulation, right: 30% NBS-12 (v/v) formulation.

#### 6.2.4. Re-melting test

To verify the reason for the samples to be white and not transparent, an additional test was carried out. A large drop of the ink with a formulation of 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume was poured on to of an alumina plate. The sample was submitted to the same thermal treatment as all of the other samples. The sample crumbled and shattered as the previous ones and the colour still remained opaque white.

The intention was to corroborate whether these results occurred because of the temperature was not high enough or the soaking time at 900 °C was insufficient. After the thermal treatment, the sample was scrapped of the alumina plate and transferred to an alumina crucible to perform a re-melting test. The crucible was put into the furnace, it was set to 900 °C and, after reaching the temperature, the crucible was let to soak for an hour. A visual inspection, performed after the hour, revealed that the sample remained unchanged. The temperature was raised to 1000 °C and the crucible was let to soak for another hour. Again, the sample remained unchanged and it was let to cool inside the furnace.

One of the pieces was taken to a stereoscopic magnifying glass for a closer visual inspection (Figure 16). The inspection revealed an irregular surface covered in cracks and holes. Yet, it was possible to observe a glass-like shine on the sample.



Figure 16. Detail of a sintered and re-melted fragment with composition of 25% NBS-12 (v/v).

## 7 CHARACTERIZATION PROPOSAL

To be able to fully understand the material synthesized and its properties, it is mandatory to undergo an extensive characterization. The process developed involves many stages, in each of those stages there are key properties which must be known and monitored precisely to accomplish an optimal final product. When the inks are formulated, it is important, beyond the rheological characterization, to understand at what point the sol-gel process finishes. While the reactions are on its course, the material is constantly changing which may induce variations in their properties when printing or sintering affecting the final product. This also implies the need to understand at which point the material could be better to print or sinter. The thermal behaviour of the material plays a major role when it is being sintering, to comprehend when the different components will volatilize allows to establish a precise thermal treatment to guarantee adequate final properties.

At last, get to know the material's internal structure and its chemical composition, give indicators of the quality of the product synthesized. Among all the existing techniques, this section will be focused on those which could provide the most information regarding the material studied and which should be the expected results.

### 7.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectroscopy (IR) is a powerful characterization technique. It works by passing infrared radiation through the sample, some of this radiation is absorbed and the other portion is transmitted. The absorption depends on the chemical bonds present in the material studied and each bond has a specific wavelength which they absorb. This phenomena produces a spectrum which is unique for each molecular structure [35].

Since each material has its own composition and its own corresponding molecular structure, IR allows to qualitatively identify every kind of material. Modern technologies also allow to perform a quantitative analysis, making possible to identify the composition of complex mixtures[35]. The main problem with this technique is the slow scanning process [35-36].

Fourier transform infrared spectroscopy (FTIR) was developed to overcome this issue. Instead of sending one individual wavelength at a time, it sends a package containing all the wavelengths encoded through a device called interferometer. This produces a spectrum called interferogram which is then decoded by means of a mathematical technique called Fourier transform. The process is carried out by computer and a regular IR spectrum is presented to be analysed. This process makes possible to test a sample in a matter of seconds in contrast to the several minutes required by the traditional IR [37].

If this technique is applied to the inks formulated, a unique spectrum will be obtained and its composition could be determined or at least inferred. However, if chemical reactions are occurring, it means new chemical bonds and structures are being created and others destroyed. This would lead to a change in the spectrum. If instead of only doing one FTIR, it is done several times at short intervals of time the result would be a changing spectrum as a function of time. After all chemical reactions reach their equilibrium, the spectrum will no longer change. In addition to a precise recording of every single reaction undergoing in the material, its composition and the quantity of the components, the time needed to complete them could also be recorded. Altogether make this an excellent technique.

## 7.2 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is a technique by which the mass loss of a material is measured as a function of the temperature. Its principle is quite simple, the instruments consists in a heating chamber, a temperature controller, a gas feeding system, a precision balance and a data analyser. The sample is placed inside a crucible (generally platinum or alumina depending on the maximum temperature desired), then, the crucible, is placed inside the heating chamber where it starts to heat the crucible. The loss of the volatiles are registered by the precision balance and the process is plotted [38-39].

Generally, two plots are given by the instrument, the proper TGA curve and the derivate which indicates the mass loss rate depending on an increase in the temperature. Modern instruments, even calculate the mass loss fraction. Furthermore, the TGA can be coupled with other instruments making it possible to characterize the gases produced by

the degradation of the sample which is also useful to determine the kinetics of a reaction [38].

In sintering processes, as the one used to obtain NBS glass, TGA is not only useful to determine the mass loss but also to establish which are the critical temperatures at which the material losses the most amount of mass. With this information, it is possible to decide the proper thermal treatment. By decreasing the heating rate and extending the soaking times at those critical temperatures, the internal tensions generated by the volatilized substance can be reduced and the distortion they generate mitigated.

Knowing the components of the inks formulated and their approximate temperature of volatilization, the shape of the TGA curve could be inferred. EtOH evaporates at 78.37 °C and water at 100 °C. Some short polymeric chains could degrade at temperatures between 200 °C and 300 °C, then the rest of the organic compounds degrade between 400 °C and 450 °C. After all the organic matter is volatilized, no further mass loss should be appreciated. Densification process, occurring at the highest temperatures (900 °C approximately), should not reflect in the TGA since they do not involve mass loss.

### 7.3 X-RAY DIFFRACTION

X-ray diffraction (XRD) is a versatile characterization technique. The information it provides is quite varied: Lattice parameters, chemical composition, macro-stresses, crystal structure, quantitative and qualitative phase analysis can be determined. To produce the x-rays, a filament of tungsten is heated in vacuum. The heating generates electron which are conducted and accelerated by high potential field where they impact a target which then emits the x-rays. This radiation emitted is characteristic of the target material [40].

Once the X-ray photon is emitted, it impacts on the material where several interactions may occur. Rayleigh scattering (a coherent, elastic scattering) is the important interaction for the XRD technique. The X-ray photons scatter in all directions and, due to the periodic nature of crystalline structures, constructive and destructive interferences occur. Those constructive interferences lead to a characteristic diffraction phenomena associated with the crystal structure of the materials.[40]

The spectrum generated is a representation of the peak intensity as function of the double angle of diffraction. The angle is associated with the periodicity of the crystalline structure, while the intensity is related to the quantity of the phases presented in the material. In vitreous materials, the absence of crystalline periodicity produces broad bands instead of peaks [40-41].

Glasses, are vitreous materials. If the formulations and the sintering were done properly, the expected result should be a single broad band, no peaks should be appreciated. Nevertheless, given the whitish colour mentioned before, it is possible that some crystalline phase have formed during the sintering stage [41].

## 7.4 X-RAY FLUORESCENCE SPECTROSCOPY

An X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for relative non-destructive tests of materials chemical compositions. It is widely used due to its great detection limit. It can detect concentrations ranging from 0.01% to 100% with high precision. And it is also able to detect materials in a wide spectrum of atomic number (from aluminium with  $Z=12$  to uranium with  $Z=92$ ) [42].

One of the main advantages is the versatility and the ease of use. Tested samples require little to none preparation in advance and it is compatible with powdered, solid and liquid samples. Also it can be performed at atmospheric conditions yielding excellent results. Furthermore, the technology has been so well developed that instruments vary from hand-held devices to table top devices, both with excellent precision and limit detection [42].

The principle by which it works, is similar to XRD. The main difference is that, instead of detecting the elastic scattering, it detects X-ray photons emitted by the transition of an electron from a higher level orbital to a lower one. X-ray radiation is emitted, it is then absorbed by the material tested, exciting it. The excited sample emits in return a mix of X-rays with a series of characteristic wavelengths proper of the atoms presented in the sample [43].

The use of this technique in the material synthesized could permit to know its exact composition. While the amounts of the reagents were thoroughly measured, it is uncertain

if all of them were incorporated into the final product. Volatilization of certain intermediate compounds could have happened, implying a change in the original composition proposed.

The main problem with the use of this technique relies on the fact that NBS glass contains boron which is under the detection limit of the technique. But, since there is only one element that cannot be detected, its concentration can be found as the difference of the total material composition and the sum of the other elements detected. The ideal result should be a composition of 80%SiO<sub>2</sub> · 15% B<sub>2</sub>O<sub>3</sub> · 5% Na<sub>2</sub>O (wt%).





## 8 CONCLUSIONS

Precursors selected (TEOS, NaOEt and  $\text{H}_3\text{BO}_3$ ) react properly to form NBS gel. The route NBS-12 is the optimal among the studied ones. The optimizations explored gave positive results. Mixing time was lowered from three to two hours and the amount of solvent was reduced to an approximate of 2% of the original amount. It is also possible to delay the gelling time indefinitely without the addition of water, which is useful to prepare large batches and store them for posterior use. It can then be affirmed that sol-gel method is suitable to form NBS glass from precursors.

Pluronic-F127, as rheological agent, has the desired rheological behaviour. An aqueous solution of 33% of PLU-F127 (w/w) loses its thermo-reversible gelation properties when it is mixed with EtOH in concentrations of 25% (v/v) and above. Instead, when it is mixed with NBS-12, higher concentrations are achievable.

The highest loaded printable ink corresponds to the formulation with a content of 75% PLU-F127 33% (w/w) + 25% NBS-12 by volume. Above this concentration, printed shapes are unable to self-sustain after printing and lower concentrations are not desired.

In summary, it is possible to produce printable NBS glass inks as a proof of concept. The sintered samples are unable to retain their given shape and the final appearance is not the expected one, however, the process developed does yield a final NBS glass piece.

For further recommendations, the use of different rheological agents should be explored to obtain even higher concentrations of NBS-12 on the formulated inks. A full characterization, as the one proposed in section 7, should be carried out to improve the final properties of the synthesized material. Finally, while sol-gel method worked, a different route could be explored to synthesize NBS glass from precursors.



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