

From polymers to covalent glasses: *a structural evolution study (PolGla)*

Abstract

Polymer-derived ceramics (PDCs) are a wide family of advanced ceramics and glasses obtained through the high-temperature pyrolysis of organosilicon polymers in a controlled atmosphere. Different compositions (SiC, SiOC, SiN, SiON, SiCN, SiBCN..., usually including also a disordered free C phase) can be obtained by tailoring the polymer chemistry, the pyrolysis atmosphere, and temperature. In particular, amorphous PDCs are of a certain interest because they offer a **unique combination of mechanical, thermal, optical, chemical, and electrochemical properties as well as high resistance to devitrification (the highest ever measured to date) and to high-temperature creep**. Moreover, PDCs can be shaped by any polymer-forming technology allowing the development of porous structures and fibers. All these features make PDCs attractive for **high-temperature structural applications, as well as high-temperature insulators, thermal barriers, and anti-corrosion/anti-wear coatings**.

Despite their technical and scientific relevance, still, **little is known about (i) how their structure evolves during the ceramization process** (when the polymer is converted into an amorphous ceramic network) **and (ii) about the medium-range order of the amorphous PDC structure**. Indeed, the local organization of the glass structure is, however, of pivotal relevance for understanding their unique set of properties and tailoring new amorphous structures.

PolGla aims at **unveiling the medium-range order and structural evolution of amorphous PDCs during ceramization**, with a specific focus on **the local arrangement of the glass-forming units, the free volume, and correlation length** (the distance over which short-range order is maintained). The study will be conducted on a model system constituted by microspheres of methyl-silsesquioxane which will be pyrolyzed in different atmospheres Ar, CO₂, Ar/H₂, and air, to obtain different glass compositions (SiOC+C_{free}, SiOC, SiO₂). **The structural evolution study during pyrolysis will be achieved by applying positron annihilation spectroscopy (PAS) to PDCs** pyrolyzed at different temperatures (i.e., with different levels of ceramization) and in different atmospheres. PAS will be carried out both through positron lifetime (very sensitive to the free volume size) and Doppler broadening studies (i.e., the broadening of the γ -rays emission due to the annihilation between e⁺ and e⁻, sensitive to the amount of *free volume*). In parallel, the materials will be studied by a set of conventional techniques such as XRD, N₂ adsorption/desorption, nuclear magnetic resonance (MAS-NMR), Raman, and Fourier-transformed infrared spectroscopy (FT-IR) and chemical analysis (Si, C, O, H) to get a complete picture of their composition, structure, microstructure, and organization of the SiX₄ units. Furthermore, the correlation length will be studied by vibrational spectroscopy, namely **low-frequency Raman spectroscopy (Boson peak position) and Brillouin scattering**.

The structural features of amorphous PDCs will be correlated to their properties. In particular, we aim at understanding the correlations between the glass structure (type, arrangement, and *free volume* of the glass-forming units and microporosity of the glass structure) with mechanical and thermal properties. The mechanical characterization will mainly involve measurements of the elastic modulus (nano-hardness tests), hardness and fracture toughness. Finally, the thermal conductivity of amorphous PDCs will be investigated by laser flash analysis (LFA) and correlated with their free volume.

In summary, *PolGla* will improve our fundamental understanding of the organic-to-inorganic transformation, will expand our knowledge of covalent glass structures obtained by PDC route, and will improve our knowledge of the correlations between PDCs structure and their thermal and mechanical properties.

1. Introduction

1.1 Polymer-derived ceramics: composition, microstructure, and properties

Polymer-derived ceramics (PDCs) are a class of advanced materials obtained through high-temperature pyrolysis in controlled atmosphere of an organosilicon resin [1]. Their main advantages reside in their highly tailorable compositions and micro/nanostructures which result in a unique combination of functional and mechanical properties. Moreover, PDCs can be produced by any polymer-shaping technique paving the way to ceramic artifacts with complex shapes as well as porous architectures.

(i) Composition and microstructural tailoring

Composition of PDCs can be controlled by tailoring the starting polymer chemistry and, accordingly, different materials can be obtained (**Figure 1a**), including SiC, SiOC, SiN, SiON, SiCN, SiBCN... The typical PDCs microstructure encompasses an amorphous matrix including a segregated carbon phase which is confined in nanodomains constituted by few sp² carbon sheets. The matrix contains tetrahedrally-coordinated Si⁴⁺ cations bonded to various anions such as 2-fold coordinated oxygen, 3-fold coordinated nitrogen, and/or 4-fold coordinated carbon.

The pyrolysis process always leads to the formation of amorphous PDCs which can eventually crystallize at high temperatures (**Figure 1b**). The crystallization process proceeds firstly through the formation of an ordered nano-domain as a result of the progressive separation of the different constituents of the amorphous solid (like SiO₂-rich and SiC-rich domains in amorphous SiOC) and their subsequent growth [2]. During the crystallization process, also the free carbon phase is partially ordered developing a graphite-like structure. Despite crystallization being the ultimate fate of amorphous PDCs, this process is usually very slow and requires extremes temperature for being activated. In this regard, PDCs offer some of the most stable amorphous solids known [3].

Interestingly, PDCs composition can be controlled also changing the pyrolysis atmosphere. For instance, the pyrolysis of a polysiloxane in an inert atmosphere leads to the formation of an amorphous SiOC matrix + C_{free} (**Figure 1a**). Obviously, if the same resin is treated in the air it is converted into SiO₂. Interestingly, Narisawa and co-workers have however shown that CO₂ and H₂ cause a preferential breakage of the Si-C and C-C bonds, respectively, thus leading in the first case to a SiO₂+C_{free} composite and in the latter to a “single-phase” amorphous SiOC [4]. The mechanistic interpretation of the CO₂ and H₂ preferential attack of the said bonds is however still not fully understood.

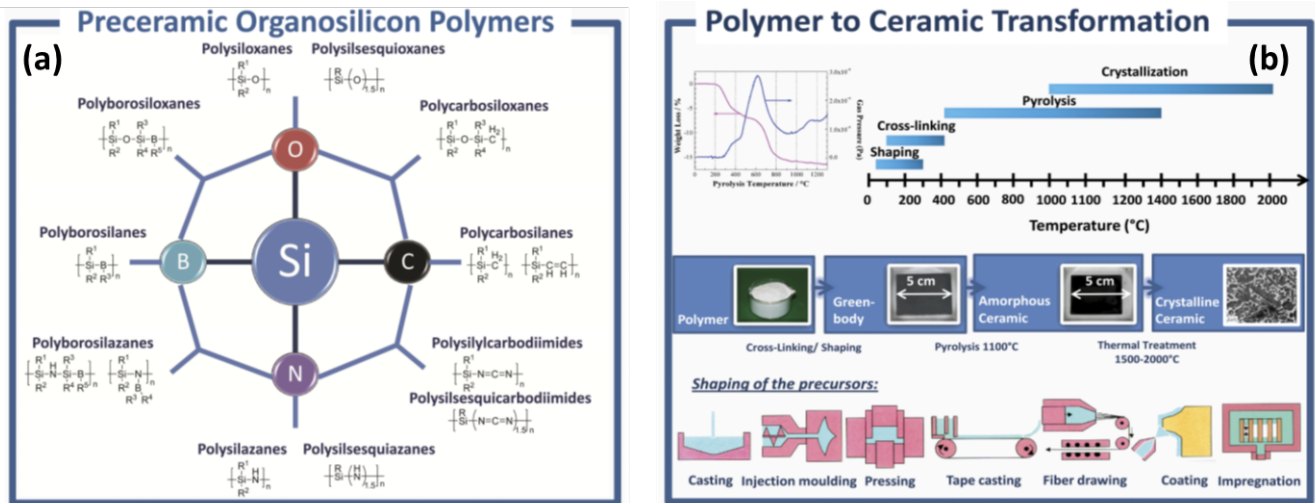


Figure 1. (a) PDCs compositions as a function of the starting polymer chemistry (pyrolysis in an inert atmosphere) and (b) processing technologies to PDCs. Taken from [1].

(ii) PDCs shaping

PDCs can be shaped by any polymer-forming technology (**Figure 1b**) like fiber spinning [5], 3D printing [6], foaming [7], tape casting [8], solution crosslinking followed by supercritical drying [9] and others. These approaches allow the development of porous architectures which cannot be easily attained (or cannot be attained at all) via the traditional ceramic processing based on powder shaping and sintering (some examples of porous PDCs developed in our lab are reported in **Figure 2**). The polymer-derived ceramic route is, therefore, an attractive approach for developing thermally stable architectures which can serve as high-temperature thermal insulators, heat exchangers, but also electrodes for alkali-ions batteries, catalytic supports, pollutant adsorbers, filters, stabilizers for phase change materials for thermal energy storage [10,11].

Finally, the polymer-to-ceramic conversion ensures, under certain conditions, the production of tapes or small components with virtually zero porosity [12]. Again, these cannot be easily obtained by powder sintering, especially considering that many PDCs compositions are refractory (SiC, SiOC, SiCN...) and their densification could be achieved only by pressure-assisted sintering (SPS or HP).

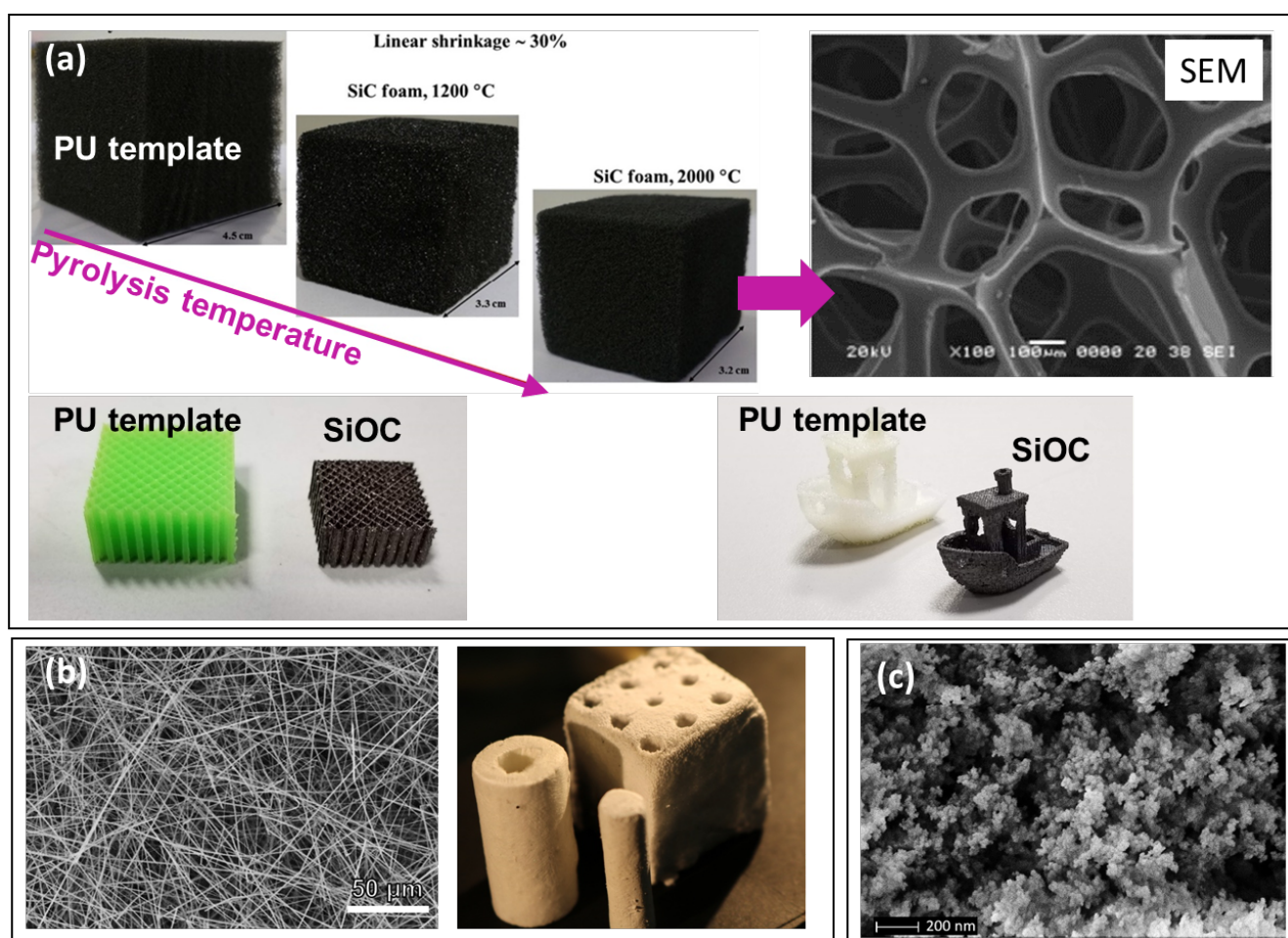


Figure 2. (a) PDCs structures obtained by replica method (impregnation of a polyurethane template with an organosilicon resin + pyrolysis); (b) polymer-derived silicon nitride nanofelts; (c) polymer-derived silicon nitride aerogels. (a), (b) and (c) are taken and adapted from [13], [14] and [15], respectively.

(iii) Properties

PDCs possess an interesting set of mechanical and functional properties which make them appealing for different kinds of applications.

First of all, their mechanical properties abundantly surpass the ones of traditional oxidic glasses in terms of Young's modulus, hardness, and crack formation probability during Vickers indentation [16]. Moreover, PDCs display the lowest Poisson's ratio (0.11) ever measured for glasses and polycrystalline ceramics [17]. These properties arise partially from the anionic substitution of C,N→O into the silica structure which increases the "volumetric bond density", N and C providing a larger number of bonds/atom compared to oxygen. On the other hand, the presence of the free carbon phase certainly plays a role as well as the PDCs medium-range structure. The latter, in particular, might be characterized by a relatively large amount of free volumes that might explain the unusually low Poisson ratio and resistance to crack formation due to the activation of densification mechanisms during indentation. However, the free volume of this class of materials as well as their medium-range order remains unexplored to date.

Other striking properties of amorphous PDCs include: (i) their high temperature creep resistance which is much larger than that of SiO₂ (higher viscosity and T_g) [18] [19], and (ii) their stability up to very high temperatures (up to 2000°C in the case of the SiBCN system [3]) without undergoing devitrification which is common in oxide glasses. The thermal stability of polymer-derived SiBCN glasses remains to date the highest ever measured. Moreover, the thermal conductivity of PDCs can be extremely low ($\approx 0.5\text{-}1\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ even at $T\approx 1000^\circ\text{C}$) [20,21], lower than that of silica, despite the presence of segregated carbon and Si-C bonds. Again, this property of PDCs might originate from their medium-range order and especially from the organization of their free volume. Finally, PDCs possess a relatively low thermal expansion coefficient ($\approx 2\text{-}3 \times 10^{-6}\text{ K}^{-1}$)[22]; and their resistance to corrosive environments (HF, caustic solutions) [23] is superior to that of SiO₂.

All these features make PDCs attractive for high-temperature structural applications, as well as high-temperature insulators, thermal barriers, and anti-corrosion/anti-wear coatings.

1.2 What do we know about PDCs structure

Amorphous PDCs can be regarded as composites containing a free carbon phase and an amorphous matrix. Their structure can be regarded as anionically substituted silica, where the O ions are replaced by carbon and/or nitrogen.

The structural evolution during the ceramization process has been investigated mostly by MAS-NMR technique [24–26][26] to identify the formation of the different silicon sites, (SiO_xC_yN_z; $x+y+z = 4$), other usual or standard characterization techniques include XRD, FTIR, Raman, and TEM. **In general, the used techniques provide information on the short-range order (first neighbors) or long-range structural organization. The information on the medium-range (a few chemical bond scales), beside few studies by Radial Distribution Function [27] and LI-TOFS [28], remains largely unexplored.**

1.3 What would we like to know?

Still, little is known about the medium-range structural organization of PDCs and about their free volume (for instance only one work is available in the scientific literature about SiOC free volume characterization [29]).

Moreover, the evolution of the said structural features during pyrolysis, when the organic part converts into inorganic, is still not understood. More importantly, the effect on the order, free volume and medium range structure of the anionic substitutions C→O into the glass network is still unknown. The local organization of the glass network is, however, of pivotal relevance. In fact, it controls the mechanical (hardness, Young's modulus, Poisson's ratio...), viscous, and thermal properties (thermal conductivity). But could also impact some electrochemical properties providing the "space" to allocate alkali ions. In this regard, our fundamental understanding of the origin of PDCs properties still needs to be clarified.

***PolGla* aims at unveiling the structural evolution of amorphous PDCs during the ceramization process, with a specific focus on the local arrangement of the glass-forming units and *free volume* evolution.**

This will allow us to:

1. Understand the transformation of organic-to-inorganic amorphous materials during pyrolysis, which is a topic much broader than the PDCs technology;
2. Correlate glass properties with its medium-range structure, paving the way to the development of optimized PDCs compositions and pyrolysis conditions;
3. Expand the knowledge about anionically-substituted oxide glasses which are an attractive class of compounds for various applications – structural components obtained by 3D printing, heat exchangers, thermal insulators, porous substrates for catalytic reactions especially in extreme environments (high-temperature and corrosive chemicals).

2. Proposed activities

To easily manage the project *PolGla* will be divided into work packages (WP) and the project development will be monitored by defining milestones. An overview of the project development is provided in the Gantt diagram at the end of the proposal.

Most of the project will be carried out at the University of Trento (UniTN) which is a recognized center for the development of polymer-derived ceramics (Prof. G.D. Sorarù/Dr. M. Biesuz group) and possess most of the facilities needed for the structural/microstructural characterization of PDCs. Moreover, the University of Trento is one of two centers in Italy possessing positron annihilation spectroscopy (PAS) for the characterization of the free volume of glasses and is a well-recognized center for this type of studies (Prof. R.S. Brusa/Dr. S. Mariuzzi group). In this regard, UniTN represents the perfect environment for the successful development of *PolGla*. Raman measurements, together with the data analysis and modeling, will be carried out at the Fluorescence and Vibrational spectroscopy laboratory of the University of Verona () thanks to the collaboration with prof. G. Mariotto and prof. N. Daldosso.

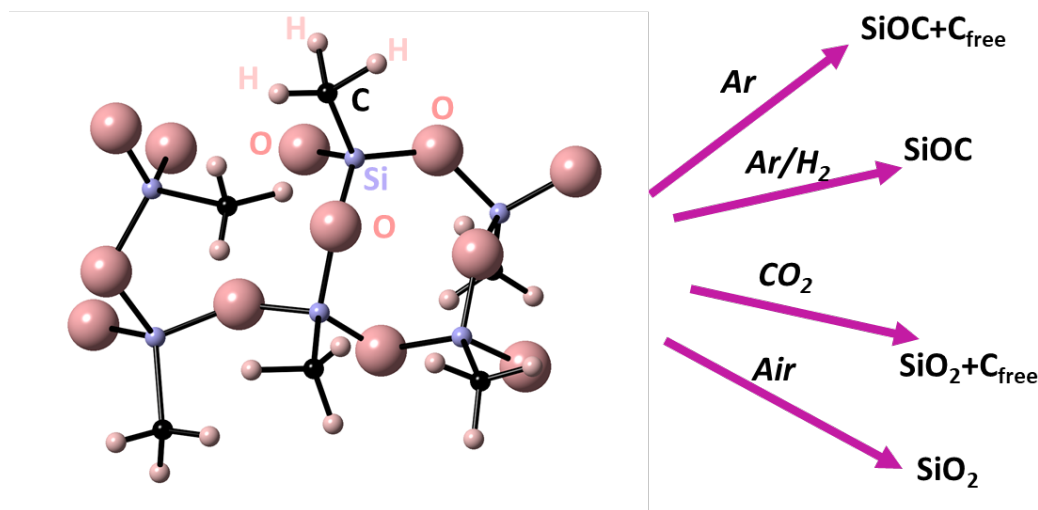


Figure 3. Methyl-silsesquioxane structure, and its evolution during pyrolysis in different atmospheres. Adapted from [33].

During the project, we will mostly focus on the PDCs obtained via the pyrolysis of a methyl-silsesquioxane. This compound is constituted by a Si-O-Si network where Si cations are coordinated by 3 bridging oxygens and a methyl group (**Figure 3**). The choice of this material is based on the fact that: (i) it can be considered a model system converting into SiOC ceramics which are by far the most studied PDCs; (ii) its pyrolysis in different atmospheres has been deeply studied [4,30], showing that we can obtain different well-defined PDCs chemistries (SiOC+C_{free} in Ar, SiOC in Ar/H₂, SiO₂+C_{free} in CO₂, SiO₂ in air). This will allow evidencing the effect of the different components on the free volume and medium-range structure of the PDCs (i.e., comparing materials with or without Si-C bonds in the amorphous matrix, or comparing materials with or without the free carbon phase...).

Other compositions (SiOCN [31] or SiBOC [32]) might be also considered for additional studies during *PolGla* if the project activities will proceed faster than the proposed reasonable schedule. This allow to expand the outcomes of *PolGla* to more complex glasses with multiple anionic/and or cationic substitution.

WP0 Literature review (month 0-1)

The project will start with a quick final check of the available scientific literature regarding the PDCs structures.

WP1 Thermal, chemical, structural and microstructural characterization (months 1-6)

Research activities

The evolution of the selected methyl-silsesquioxane during pyrolysis in different atmospheres and at different temperatures (\approx RT-1400°C) will firstly be characterized using the most established techniques for the PDCs characterization. To ensure a complete reaction (if any) between the atmosphere and the pre-ceramic compound the work will be mostly carried out on microspheres.

In detail, the thermal behavior during pyrolysis will be monitored by TGA/DTA (also coupled with mass spectroscopy) and dilatometric tests. This will allow following the reactions taking place during pyrolysis (often related to weight loss due to the evolution of the organic part of the compound). The presence of micro- or mesopores will be investigated by gas physisorption isotherms, and by TEM. TEM will also allow getting morphological information about the structure of the segregated carbon phase which will be further deepened by vibrational spectroscopy. The formation and disappearance of chemical bonds will be studied by FTIR and Raman spectroscopy. The PDCs density will be characterized by He picnometry. The evolution of the chemical environment of Si will be investigated by NMR. Finally, the presence of long-range ordering will be checked by XRD and SAED.

The chemical composition of some PDCs will be carried out by combustion and fluorescence analysis, which will be purchased from a specialized laboratory (Mikroanalytisches Labor Pascher, D-53424 Remagen, Germany).

At the end of this WP, the long (XRD) and short range order (NMR, Raman, FTIR) of the selected materials will be completely characterized and the results will serve as a solid background to study the medium-range features that will be deepened in the following WPs.

Milestones

M1.1 Complete thermal, chemical, structural and microstructural characterization of methyl-silsesquioxane pyrolyzed at 4 different temperatures in 4 different atmospheres (Ar, Ar/H₂, CO₂, Air). The pyrolysis temperature choice will be carried out based on the thermal analysis (WP1).

Research risks

This activity does not contain particular risks as it is based on well-established techniques for PDCs characterization. The main possible issues are related to the failure of some equipment. If this will be the case, we will seek a quick repair of the facilities also taking advantage of some internal services to our institution (for instance there is a group taking care of repairing electronic facilities). If a quick solution will not be possible we will seek external analysis.

WP2 Inside the PDCs structure by vibrational spectroscopy (months 3-15)

Research activities

PolGla will investigate for the first time the PDCs structure and the ceramization process via low-frequency Raman and Brillouin scattering. The combination of these techniques will allow the determination of (i) the evolution of transversal and longitudinal sound velocity on PDCs during ceramization; (ii) the position and the intensity of the

Boson peak. The Boson peak represents a low energy excess in the vibrational density of states $g(\omega)$ over the Debye prediction, resulting in a deviation of both the heat capacity/ T^3 and the $g(\omega)/\omega^2$ (for any amorphous solid). It represents a fingerprint of the glass intrinsic disorder and allows the determination of the glass correlation length (ξ) [34–37], which is the distance over which the short-range order is maintained (i.e., the pair distribution function does not $\rightarrow 0$, see **Figure 4a**):

$$\xi = \frac{v_T}{\omega_{BP}} \quad (1)$$

v_T being the transverse sound velocity and ω_{BP} the Boson peak frequency. An example of the application of Eq. 1 is reported in **Figure 4b** for binary alumina-silica glass.

The identification of the Boson peak in SiOC-based ceramics will allow an understanding of the role of the anionic substitution C→O on the “order” of the glass structure. Such studies have been already carried out in oxidic glasses characterized by cationic substitution, however, no reports on systems including carbon anions have been reported to date. The possible relation between the “order” of the glass structure (correlation length) will be correlated with the size and amount of free volumes [38,39] that will be studied in WP3 and with the local environments of Si (identified by NMR in WP1). As such, **PolGla will improve our fundamental understanding of the glass state with a specific focus on glass systems of particular interest for high-temperature applications.**

The information about the SiOC ordering at the medium scale via Boson peak scaling procedure will also provide information on the progressive evolution of the elastic medium SiOC→SiC+SiO₂, as well as monitoring the incursion of phase separation which is relevant for the activation of the de-vitrification process. In other words, it will provide a tool to monitor the nucleation of crystals in the early stages of crystallization in anionically-substituted glasses. The scaling would assess the chemical limit at which it may occur.

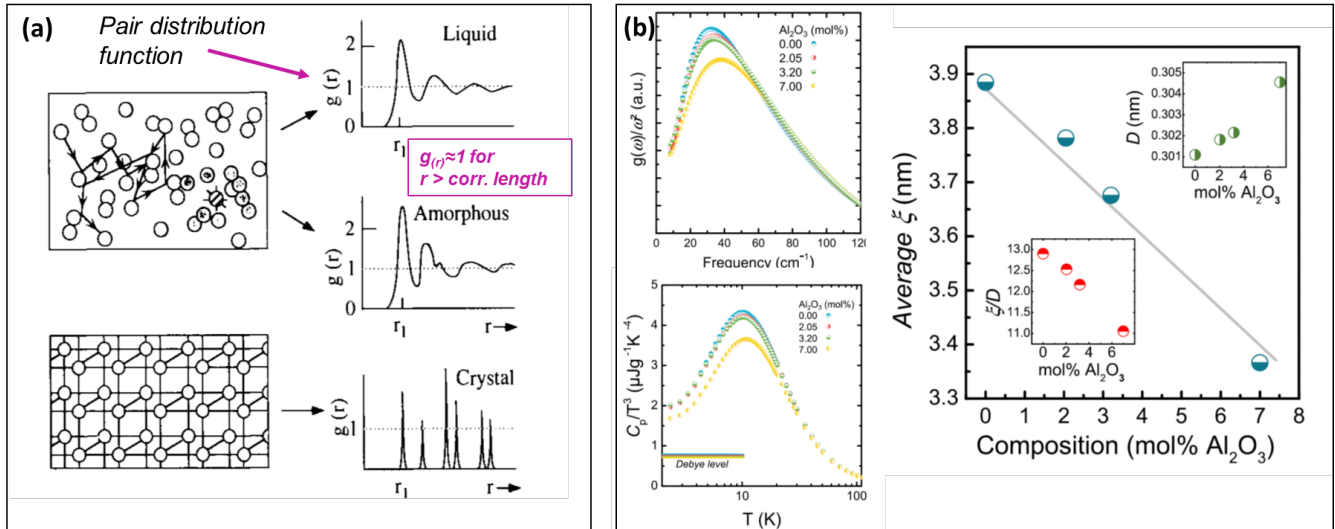


Figure 4. (a) Schematic representation of crystals and glass structures and related pair distribution function. Adapted from [40]. (b) Boson peak determined by low-frequency Raman spectroscopy and its effect on the low-temperature C_p with the frequency and temperature scalings and correlation length (ξ) of binary silicate-aluminate glasses. Taken from [36].

The determination of the boson peak position and sound velocity is finally relevant for the identification of some properties of this class of materials. For instance, we will be able to identify the Poisson’s ratio (ν) from the sound velocities [37]:

$$\nu = \frac{v_L^2 - 2v_T^2}{2(v_L^2 - v_T^2)} \quad (2)$$

v_T and v_L being the transverse and longitudinal sound velocity. The low value of Poisson's ratio is a key feature of SiOC and relates also to their resistance to crack formation [41] (**Figure 5a**). Its evolution as a function of the pyrolysis stage has not been studied yet and could be also correlated to the amount of free volume in the solid (studied in the next WP). Starting from v_T and v_L all the other elastic properties can be determined, including the shear (G) and elastic modulus (E). The study of the different elastic properties and the pyrolysis atmospheres will allow a correlation of the effect of anionic substitution on the mechanical performances of glasses.

Finally, relations have been proven to exist between the bulk (K) and shear (G) modulus (K/G) (i.e. retrievable from the sound velocities), the Boson peak, and the melt fragility [42,43]. As such, *PolGla* will provide the preliminary foundation for the determination and validation of models for studying the temperature dependence of viscosity and creep of PDCs at high temperatures.

Milestones

M2.1 Identification of the Boson peak position in PDCs obtained from methyl-silsesquioxane at 4 different pyrolysis temperatures and 4 different atmospheres.

M2.2 Identification of the sound velocity (Brillouin scattering) in PDCs obtained from methyl-silsesquioxane at 4 different pyrolysis temperatures and 4 different atmospheres.

M2.3 Identification of the elastic properties, melt fragility, and correlation length (and local order) for the said set of materials.

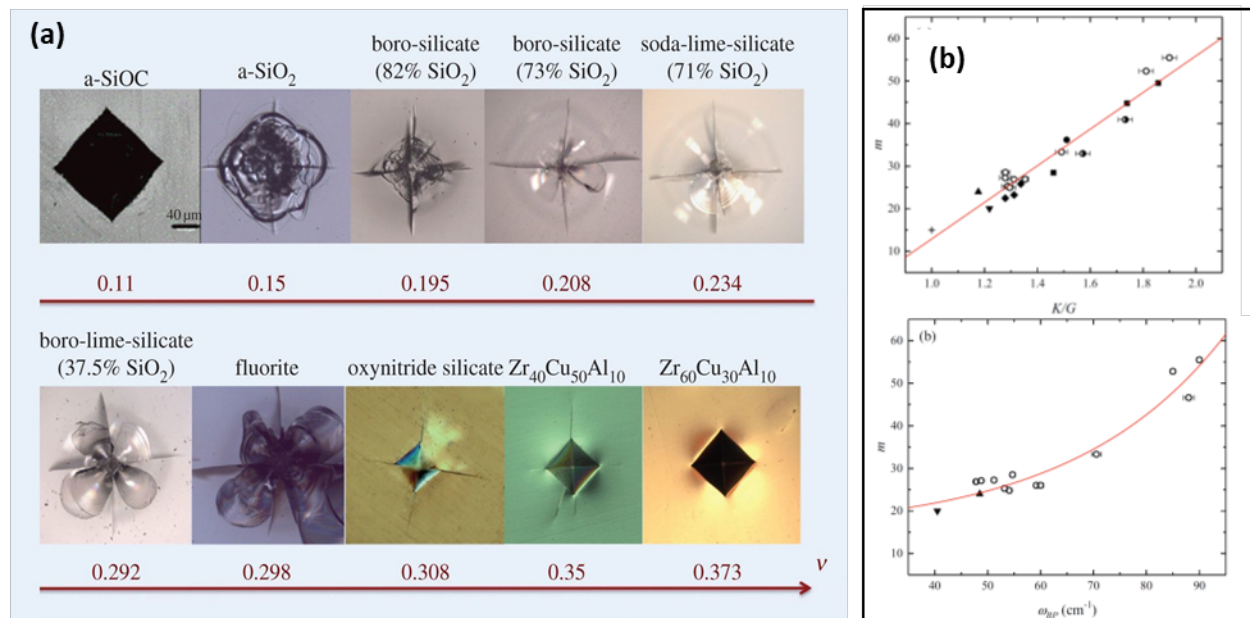


Figure 5. (a) Crack formation after Vickers indentation in glasses with different Poisson's ratio (taken from [41]). (b) Relation between elastic properties, Boson peak position and melt fragility, m (Taken from [42]).

The activities proposed in WP2 are totally new and therefore are associated with medium/high research risks.

The main risk is related to the possible fluorescence related to point defects and C nanocrystals within the SiOC matrix. Fluorescence might interfere with the observation/detection of the Boson peak position. As mitigation action, we will use different excitation lasers to seek an energy window minimizing fluorescent effects. If the problem will persist then we will (i) look for other approaches for measuring the Boson peak frequency (for instance by low-temperature calorimetry); (ii) we will focus on systems pyrolyzed at temperatures high enough to cause defects annihilation.

In the unlikely case that we will not be able at all of determining the Boson peak position, then we will anticipate the beginning of WP3 and expand the free volume study (see WP3) to different classes of PDCs (like SiOCN, SiBOC...).

WP3 Free volume of PDCs (months 15-32)

Research activities

We will characterize the free volume of polymer-derived glasses by positron annihilation spectroscopy (PAS). **PAS (Figure 6) is an advanced tool [44,45] for the identification and quantification of structural voids in solids at the Ångstrom and nanoscale** (not detectable by N_2 physisorption). A positron beam strikes the sample and the positron gets preferentially trapped into “structural voids” due to the electrostatic repulsion between e^+ and the atomic nuclei. Information about the “void” size and concentration can be derived from the positron lifetime in the sample, τ , and from the Doppler broadening of the γ -ray emission signaling the positron annihilation with the electron ($2\text{-}\gamma$ emission at $511 \pm \Delta E$ keV). Since the annihilation probability is inversely proportional to the volume integral of the positron and electron density product, the larger the void the longer the lifetime is. Hence, positron lifetime annihilation spectroscopy (PALS) provides detailed information about the free volume size and concentrations. On the other hand, Doppler broadening is related to the momentum of the electron the positron annihilates with (being the positron thermalized, $E_{kin\ e^+} \approx kT$, its kinetic energy is negligible). ΔE is larger when the annihilation occurs with core-shell high-momentum electrons, compared to valence low-momentum electrons (**Figure 6**). Since the density of core electrons in structural voids drops more than that of valence electrons, the Doppler effect allows an indirect observation of the presence of point defects and free volumes (though with a lower sensitivity to the defect type compared with PALS). Whereas lifetime studies require that only one positron exists in the material at a given time (it is required to define a t_0 corresponding to the positron birth and therefore needs a pulsed positron beam), the Doppler effect study can be carried out with continuous beams, thus being much easier and faster than PALS.

Indeed, other techniques like HR-TEM could be used to observe the Si-X “rings” constituting the free volume of the glass structure. However, PAS has some clear advantages: (i) it samples a “large portion” of the material ($\approx 10^5 \mu\text{m}^3$) whereas TEM allows the observation of only limited regions; and (ii) the absence of sample preparation in PAS (cutting, etching, ion milling et cetera are required before TEM) ensures that the measured features are not artifacts.

Therefore, using PAS we will be able to provide a quantitative report of the free volume size, amount, and distribution in PDCs pyrolyzed at different temperatures and in different atmospheres. This will provide some new useful **information to rationalize their mechanical and thermal properties** (which are identified by WP2 and 4) and **to understand the effect of anionic substitution on the glass structure**. This will take advantage of the pyrolysis processes in different atmospheres that lead to different compositions and chemical environments of silicon. For instance, by comparing the results obtained in air (SiO_2) and Ar/ H_2 (SiOC w/o C_{free}) we will be able to underline the effect of the anionic substitution on the glass network.

Indeed, we will also seek for correlations between the size/amount of free volumes, the diffraction peak position (WP1), see for instance [38], and the different degree of “ordering” (correlation length) of the glass structure (WP2).

PAS will provide information on the thermal stability of the PDC glass architecture and its possible densification upon heating: we expect that the structure of polymer-derived glasses after low-temperature ceramization is more disordered and open and partially close and rearranged upon heating, at least up to a certain temperature. The results regarding the free volume of PDCs will be correlated with the density measurements and chemical composition determined in WP1 to get a complete and robust picture of the ceramization process.

It is noteworthy that the PAS studies could also improve our fundamental understanding of

- (i) The organic-to-inorganic transformation: it will provide details about the structural re-organization of the network while losing the organic species that evolved in the gas phase,

- (ii) The mechanisms of the reaction between pre-ceramic resins and reactive atmospheres (Ar/H₂, CO₂) which is still not understood.

Finally, using positrons possessing different energies we will be able to check/probe whether or not the PDCs structure in the bulk is different from the one on the surface. Some differences might actually originate during the ceramization as a result of the different diffusion lengths for the pyrolysis gases evacuation (i.e., the gases produced by the decomposition of the organic part). This might explain some results obtained by our group a few years ago on surface/core gradients in the mechanical properties of PDCs [46].

Milestones

M3.1 PAS Doppler broadening of PDCs obtained from methyl-silsesquioxane at 4 different pyrolysis temperatures and 4 different atmospheres.

M3.2 Determination of the free volume size distribution by PLAS of methyl-silsesquioxane PDCs pyrolyzed at (at least) 8 selected combinations of pyrolysis temperature/atmosphere.

Research risks

Similar to WP1, WP3 does not show significant research risks. PAS is a quite well-established technique and UniTN is a well-known center operating with this characterization tool. Despite this project reporting its first application to PDCs, we trust that no particular issues will emerge during the project.

The main risk is again associated with equipment failure. In the case of that unlikely event, we will benefit from Dr. Mariazzi's research network for operating some analysis outside our institution.

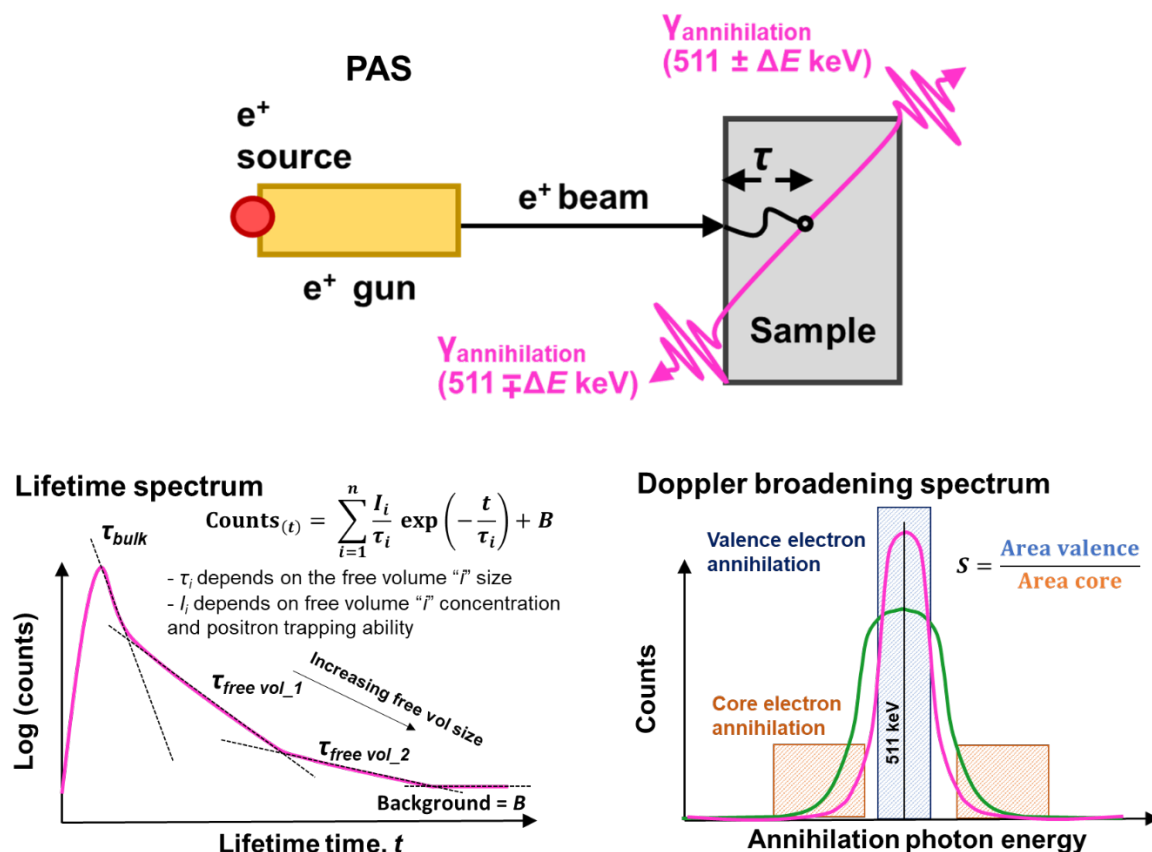


Figure 6. Schematic representation of PAS, lifetime spectrum (each lifetime, τ , is associated with a specific free volume size), and Doppler broadening spectrum.

WP4 Thermal and mechanical properties of PDCs (months 24-36)

Research activities

The results obtained in WP2 and WP3 about the PDCs medium-range structure will be used to rationalize some of their properties. In this regard, we are planning to measure the elastic modulus of the PDCs obtained at different pyrolysis conditions (temperature/atmosphere) by nano-indentation. These results will be compared with the estimations of the elastic properties calculated in WP2. Nanoindentation will allow also us to evaluate the hardness evolution during pyrolysis as a function of temperature and of the atmosphere and will allow building hardness maps to check whether their surface shows feature different from the bulk (because of the different evacuation rate of the gasses produced during pyrolysis).

We also plan to measure the fracture toughness and crack formation probability of PDCs by Vickers indentation. This will require the production of some monoliths which will be obtained by forcing the densification of the pyrolyzed powders by high-pressure spark plasma sintering. Indeed, we target to carry out the PDCs densification at temperatures lower than that used for pyrolysis to produce only limited structural evolution in the sintering step. In order to reduce microstructural effects on the measured properties, we will consider only monoliths with a relative density >98%. This part will take advantage also of the long experience of Dr. M. Biesuz in the field of ceramics sintering.

Finally, the thermal conductivity of amorphous PDCs will be investigated by laser flash analysis (LFA) and correlated with their free volume. Again, these tests will be carried out on monoliths.

Besides the relations we will build between PDCs structure and their properties, the results achieved WP4 will allow also us to clearly evidence the effect of the different PDCs components (anionic substitution, presence of free carbon...) on the mechanical and thermal performances of these materials.

Milestones

M4.1 Nano-indentation (hardness maps and elastic modulus) of PDCs obtained from methyl-silsesquioxane at 4 different pyrolysis temperatures and 4 different atmospheres.

M4.2 Obtaining monoliths (density > 98%) out of PDCs powders by high-pressure spark plasma sintering at temperatures lower than the pyrolysis one.

M4.3 Crack formation probability and fracture toughness determination of the said monoliths.

M4.4 Thermal conductivity measurement of the said monoliths.

Research risks

Excluding the obvious risks related to equipment failures, the main research risk related to WP4 is associated with the production of the monoliths (density >98%) at temperatures lower than the pyrolysis one. The use of pressure-assisted densification should, however, hugely mitigate this risk as it will hugely reduce the consolidation temperature. If we will not be successful the following contingency action will be considered: (i) we will consider accepting a sample with a relative density down to 95%; (ii) we will focus only on the samples obtained at the highest pyrolysis temperatures (for which pressure-assisted sintering should be completed before reaching the pyrolysis temperature).

WP5 Results dissemination (months 3-36)

The relevant result will be disseminated by oral presentations at international scientific conferences (3 conferences over 3 years) and publishing manuscripts in international peer-reviewed scientific journals (we target at least 5 journal articles).

The main results as well as the development of the project and the AFOSR (Air Force Office of Scientific Research) contribution will be advertised by using our social media networks and those of our labs (mainly on LinkedIn and ResearchGate) and via the institutional website of UniTN and its departments.

WP6 Project management (months 0-36)

To easily check the project progress and activate the said contingency plans/risk mitigation actions, we have defined several milestones (see previous WPs) which are introduced in the Gantt diagram of the activities (Figure 7).

To continuously check the experimental results and propose immediate actions we plan to schedule a meeting between the PI and the post-doctoral researcher hired on the project every 2 weeks. Moreover, a general meeting including all the students/researchers involved in the project will be scheduled every 3 months. We also plan to keep our reference person at AFOSR updated every ≈ 3 months about the project status and results.

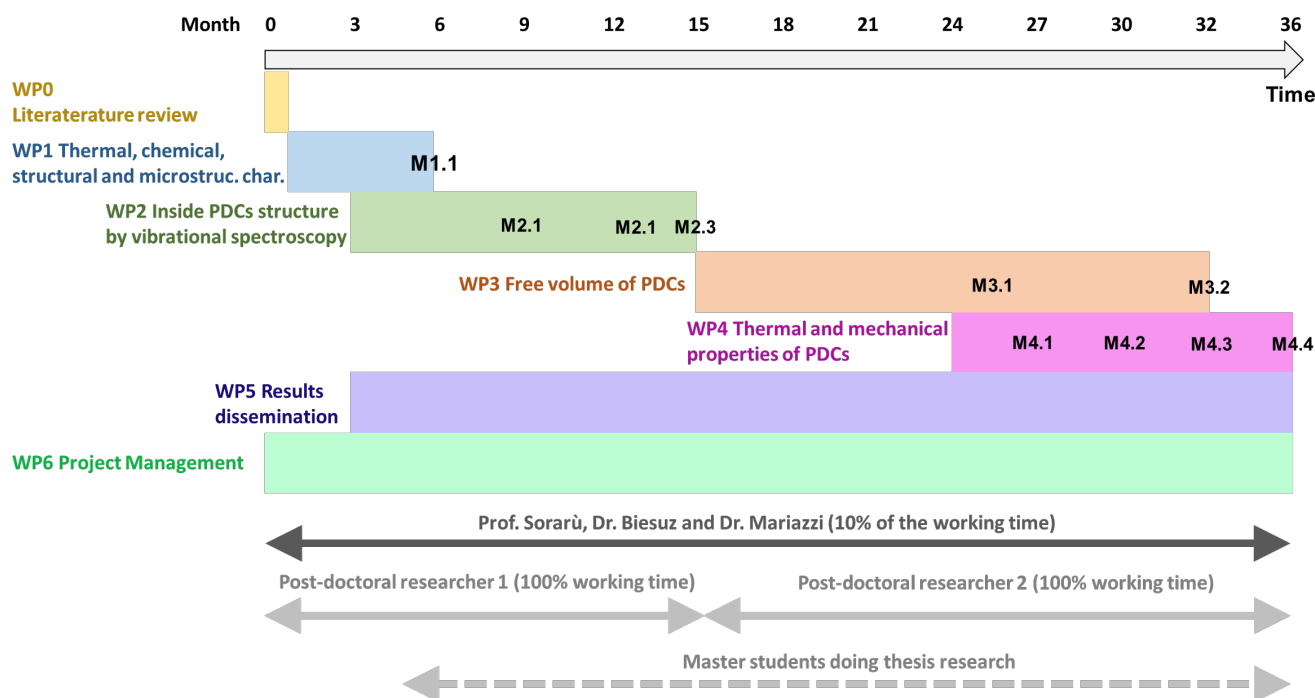


Figure 7. Gantt diagram of the project.

Human resources

The project will involve the PI, Prof. G.D. Sorarù, and 2 researchers, Dr. M. Biesuz and Dr. S. Mariazzi, who will work on the project for 10% of their working time (average over 3 years).

Within *PolGla* project, we will pay 3 years of post-doctoral fellowship(s) (100% of the working time). This will be probably divided between 2 different researchers (see the Gantt diagram) as different expertise will be needed: the first one will focus mostly on the vibrational spectroscopy part (WP1-2, month 0-15), whereas the second will focus on PAS and mechanical/thermal properties measurements (WP3-4, year month 15-36). The scientific continuity of the project will be anyway ensured by the PI and the permanent researchers.

Indeed, we also plan to involve young master students in *PolGlas* within their master thesis research activities. These will help the post-doctoral researcher carry out some experimental work in the lab and might allow expanding the studies to different PDCs compositions.

3. Conclusions

In summary, *PolGla* will improve our fundamental understanding of the organic-to-inorganic transformation, will expand our knowledge of covalent glass structures obtained by PDC route, and will improve our knowledge of the correlations between PDCs structure and their thermal and mechanical properties.

This class of materials due to their unique combination of properties (thermal stability, corrosion resistance, creep resistance, good mechanical properties, low thermal conductivity) and the possibility of obtaining complex and porous architectures, is of certain interest for several applications relevant to the defense field and aerospace industry (thermal insulators for high temperature, thermal barriers, heat exchangers, structural components, anti-oxidation/wear coating...). As such, we trust that ***PolGla* will put a step forward in our understanding and possibility of designing advanced materials of broad interest for AFOSR.**

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