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Ph.D. Thesis in Industrial Product and Process Engineering XXXIV cycle

# DEVELOPMENT OF INNOVATIVE ELECTROSPUN COMPOSITES VIA SOL-GEL PROCESS

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# **Thesis Overview**

#### Everything is made of something.

Material science represents a branch of the natural sciences that becomes crucial in a world dominated by the importance of the choosing of suitable material. New materials are required for a wide variety of applications, which have to be extremely specialized and at the same time sustainable and economically affordable. High technology materials are required in every technological field, ranging from opto-electronics or biomaterials for medical application to adsorbent materials, and they must be designed or invented with great care.

In this scenario the use of hybrid materials opens new routes to the production of innovative materials, whose properties can be tailored depending on the demands for the different applications. Their properties, in fact, can be chosen so as to obtain the best performances of the organic materials and the inherent stability of the inorganic ones. In particular, when the two phases are structured on a micro- and nanometer scale, the result can be considered as a new material with desired properties and a structure that can diverge from those of the starting components, so called: "composite material".

In the last decades, the use of composite hybrid materials has appeared crucial in many fields of application (e.g. building engineering, naval engineering, aerospace, high tech industries etc.); therefore there has been a intensive increase of interest in the chemical procedures needed for their fabrication.

The sol-gel synthesis route has been extensively exploited since the 1970s, in combination with polymer synthesis methodologies, to produce not only inorganic materials (glassy or ceramic) but also hybrid organic/inorganic (O/I) composites in the form of aerogels, monoliths, coatings, fibers, and particles. The strategy takes advantage of the fact that almost all the important oxides MOn (where M is a metal or semimetal and n is not necessarily an integer), as well as many mixed oxides, have been prepared by the sol-gel process through reactions occurring at low temperatures starting from precursors that are commercially available at high purity. Sol-gel synthesis also allows the easy production of particles at the nanoscale, where materials properties change. Moreover, the sol-gel process has been extensively employed as the most important route in tailoring textile surfaces and in forming new hybrid inorganic–organic materials. This is because this process can modify the chemical nature of material surfaces and introduce ceramic phases into composites through chemistry. Very mild

reaction conditions and low reaction temperatures are particularly useful for incorporating inorganic filler into organic materials or organic materials into inorganic matrices.

The aim of this PhD project was to show the use of sol-gel chemistry in the development of innovative electrospun composites materials for relevant industrial applications.

In this work the sol-gel methodology has applied to solve some technological problems inherent to the use electropsun polymer composites for industrial and environmental applications.

The electrospun fibers have become very interesting topic for the researchers due to their applications ground, and they have been used in various research fields such as industrial, biomedical, electrical & electronics, environmental and energy resources due to their advanced properties and high potentials applications.

However, these electrospun mats can show some limitations. For example, low resistance to organic solvents and thermal instability (i.e. shrinkage) of the fiber; or easy flammability of the polymer matrix that can significantly restrict the application fields of these materials. This latter issue, is of particular importance especially in the aerospace industry where the introduction of new material is dictated by specific regulation. In fact, often fire tests have to be passed by the new material, in order to guarantee public safety and be compatible with the aerospace application.

Sol-gel methodologies can improve the fire behavior, the resistance to organic solvents and thermal stability of electrospun polymer composites through the use of sol-gel particles added into polymer solution.

Therefore, this PhD thesis covered the series of experiments related to electrospun composites for aerospace and environmental applications. For this purpose, the incorporation of sol-gel nanoparticles with a biocompatible polymer to the formation of blended micro and nanofibers was started. The novelty of this work relies on the use of a biocompatible polymer namely poly (vinyl pyrrolidone) (PVP), which has a great interest in recent years. The successful fabrication of novel electrospun fibers using high content of silica sol-gel nanoparticles incorporated in PVP for aerospace applications it was reported. On the basis of characterizations results, it was concluded that PVP/SiO<sub>2</sub>Np electrospun composites are more suitable for sound adsorption properties, in the lower frequency range, as compared to other materials (e.g. glass wool) normally

used as fuselage coating in aircrafts. Moreover, PVP/SiO<sub>2</sub>Np electrospun composites showed an excellent fire barrier property due to the presence of silica sol-gel nanoparticles.

Regarding environmental applications, novel PVP-based ternary electrospun composite mats containing silica sol-gel nanoparticles (SiO<sub>2</sub>Np) and sol-gel TiO<sub>2</sub>-acetylacetonate (TiO<sub>2</sub>acac) microparticles (up to 90  $\mu$ m) it is also reported. The presence of hybrid titania made this ternary electrospun composites a promising membrane for adsorption/degradation of water pollutant in absence of light irradiation.

This work is structured in the following six chapters:

In Chapter 1.0 the fundamentals of sol-gel chemistry, with particular attention to metal oxides particles such as silica and titania are reported.

In Chapter 2.0 the main aspects of the electrospinning process and its applications in the industrial field are explained.

In Chapter 3.0 it is reported the state of art of this work and its objectives. In particular the importance of using electrospun composite materials in aerospace or environmental applications is emphasized. The reason why it was decided to produce electrospun composite materials by incorporating sol-gel particles is then reported.

In Chapter 4.0 materials and methods employed to produce and characterize the electrospun composite samples PVPSi and PVPSi\_Tiacac are listed.

In Chapter 5.0 and Chapter 6.0 are discussed the promising results obtained for both samples. In particular, the successful fabrication of novel polymer electrospun fibers using silica sol-gel nanoparticles for aerospace applications and also using titania particles for removal of pollutants are reported in detail.

### 1.0 The Sol–Gel Process: fundamentals

Sol-gel materials are therefore metastable solids that are formed in kinetically controlled reactions from molecular precursors, which constitute the building blocks for the later materials. An immediate consequence is that all reaction parameters, including the precursor properties, have a decisive influence on the structure and thus the properties of sol-gel materials [Brinker 1990]:

• a sol is a stable suspension of colloidal particles (nanoparticles) in a liquid. The particles can be amorphous or crystalline, and may have dense, porous, or polymeric substructures. The latter can be due to aggregation of sub-colloidal chemical units;

• a gel consists of a porous, three-dimensionally continuous solid network surrounding and supporting a continuous liquid phase ("wet gel"). In most sol–gel systems for the synthesis of oxide materials, gelation (i.e., formation of the gels) is due to the formation of covalent bonds between the sol particles. Gel formation can be reversible when other bonds are involved, such as van der Waals forces or hydrogen bonds. The structure of a gel network depends to a large extent on the size and shape of the sol particles.

The easy agglomeration or aggregation of fine particles (sol particles) is caused by attractive van der Waals forces and/or minimization of the total surface or interfacial energy of the system. In order to prevent aggregation (i.e., to stabilize the sols), repulsive forces of comparable dimensions are required that must be overcome during gelation. Stabilization can be achieved by adsorbing an organic layer ("steric barrier") or by creating electrostatic repulsion between the particles. This shows the great influence of organic additives and especially ionic species on the gelation behavior, as will be discussed later in more detail. The stability and coagulation of sols is of utmost importance to sol–gel chemistry. Gelation can also be induced by rapid evaporation of the solvent, which is especially important for the preparation of films or fibers. Drying of the initially obtained wet gels by evaporation of the pore liquid gives rise to capillary forces that cause shrinkage of the gel network, often by a factor of 5–10. The resulting dried gels are called xerogels. Due to the drying stress, monolithic gel bodies are often

destroyed, and powders are obtained. When a wet gel is dried in a way that the pore and network structure of the gel is retained, the resulting dried gel is called an aerogel.

In the following, the chemical and physical principles behind the individual steps of solgel processing will be discussed in more detail.

#### **1.1 Hydrolysis and Condensation Reactions**

#### 1.1.1. Silica-Based Materials

The basic chemical principle behind sol–gel processing of silica-based materials is the transformation of Si-OR and Si-OH containing species to siloxane compounds by condensation reactions. From a structural point of view, this corresponds to connecting SiO4 tetrahedra (or RSiO<sub>3</sub> tetrahedra in hybrid materials) by corner sharing. To obtain a stable gel, the number of siloxane bonds (Si-O-Si) must be maximized and consequently the number of silanol (Si-OH) and alkoxy (Si-OR) groups has to be minimized.

The most common precursors are aqueous solutions of silicates ("water glass") and silicon alkoxides, Si(OR)<sub>4</sub>, mostly tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). Water glass solutions contain complex mixtures of different monomeric and oligomeric silicate species (i.e., species with negatively charged, nonbridging oxygen atoms), with an approximate average composition of M<sub>2</sub>SiO<sub>3</sub> (M=Na, K). The equilibrium compositions of such "metasilicate" solutions are highly dependent on the concentration, pH, metal counterion, temperature, and so on. The point of zero charge (PZC) of Si-OH-containing species is between pH 1.5 and 4.5; the higher the degree of condensation of the silica species, the lower the PZC (the acidity of surface M-OH groups generally depends somewhat on the particle size). Acidifying a solution to a pH below the PZC means that the siliceous species are positively charged (Eq. (1.1) and Eq. (1.2)). The silicate species in water glass solutions are stable only under strongly alkaline conditions, because the anionic species reject each other.

$$Si-OH + H^+ \rightarrow Si-OH_2^+ \tag{1.1}$$

$$Si-OH + OH^{-} \rightarrow Si-O^{-} + H_{2}O$$
(1.2)

The chemical reactions during sol-gel processing can be formally described by three equations (Eq. (1.3), Eq. (1.4) and Eq. (1.5)). In alkoxide-based systems, hydrolysis reactions of Si-OR groups must precede condensation to generate the Si-OH groups, which are necessary for condensation. The fact that the reactive groups must be created

in the first place is an important difference to typical organic polymerization reactions. Condensation (i.e., formation of Si-O-Si units) takes place by either alcohol or (more often) water elimination.

$$\equiv \text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{ROH}$$
(1.3)

$$\equiv \text{Si-OR} + \text{SiOR} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{ROH}$$
(1.4)

$$\equiv \text{Si-OH} + \equiv \text{SiOH} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O}$$
(1.5)

The most important differences between the two precursor types are the following:

• Gelation is initiated in aqueous silicate systems by pH changes, and in alkoxide precursor systems by addition of water (hydrolysis reactions to generate Si-OH groups).

• A mixture of a Si(OR)<sub>4</sub> in water and alcohol would react very slowly. Therefore, acid or base catalysis is necessary to start the hydrolysis and condensation reactions of alkoxysilanes.

• The solvent in water glass-based reactions is always water, while the alkoxides are employed either neat or dissolved in an organic solvent. Since many alkoxysilanes are immiscible with water, alcohols are often used to homogenize the reaction mixture (mostly the same alcohol as liberated by the hydrolysis reactions to avoid alcohol exchange reactions).

• Alkoxide-based systems are more complex because more parameters influence the sol–gel reactions. This gives more possibilities to control the texture and properties of the obtained materials.

The use of silicon alkoxides also allows introducing organic groups, by means of organo-substituted derivatives. While sol–gel processing of tetraalkoxysilanes, Si(OR)<sub>4</sub>, results in the formation of silica, SiO<sub>2</sub>, alkoxysilanes of the type R'Si(OR)<sub>3</sub> (R'= any hydrolytically stable organic moiety) result in the so-called silsesquioxanes, R'SiO<sub>3/2</sub>. In practice, however, alkoxysilane mixtures are processed in most cases, by which any proportion of the organic group(s) R' can be introduced.

The reaction mechanisms are the same for both silicate and alkoxysilane precursors. However, from a mechanistic point of view, reactions under acidic or basic conditions have to be considered separately. Under acidic conditions, that is, at a pH below the PZC, the oxygen atom of a  $\equiv$ Si-O-,  $\equiv$ Si-OH, or  $\equiv$ Si-OR group is protonated in a rapid first step (see Figure 1). A good leaving group (water or alcohol) is thus created. In addition, electron density is withdrawn from the central silicon atom, rendering it more electrophilic and thus more susceptible to attack by water (in hydrolysis reactions) or silanol groups (in condensation reactions).



Figure 1: Sol-gel reactions under acid conditions [Brinker 1990].

Under basic conditions, the reaction proceeds by nucleophilic attack of either an OH-(in hydrolysis reactions) or a  $\equiv$ Si-O<sup>-</sup> ion (in condensation reactions) to the silicon atom with an S<sub>N</sub>2-type mechanism (see Figure 2). The entering OH<sup>-</sup> or  $\equiv$ SiO<sup>-</sup> group is formed by deprotonation of water or a  $\equiv$ Si-OH group. Under strongly alkaline conditions, the Si-O-Si bonds can be cleaved again by OH<sup>-</sup>.



Figure 2: Sol-gel reactions under basic operative conditions [Brinker 1990].

Inductive effects of the substituents attached to a silicon atom are very important, because they stabilize or destabilize the transition states or intermediates during hydrolysis and condensation. The electron density at the silicon atom decreases in the following order:

$$\equiv \text{SiO-R'} \ge \equiv \text{SiO-OR} \ge \equiv \text{SiO-OH} \ge \equiv \text{Si-O-Si}$$
(1.6)

For acid catalysis, the electron density at the silicon atom should be high because the positive charge of the transition state (Figure 1) is then stabilized best. Therefore, the reaction rates for hydrolysis and condensation under acidic conditions increase in the same order as the electron density. For base catalysis, a negatively charged intermediate has to be stabilized (Figure 2). Therefore, the reaction rates for hydrolysis and condensation increase in the reverse order of the electron density.

This has several consequences, for example:

• As hydrolysis and condensation proceed (increasing number of -OH and -OSi units attached to a specific silicon atom), the silicon atom becomes more electrophilic. This means, for example, that in acidic media monomeric  $Si(OR)_4$  hydrolyzes faster than partially hydrolyzed  $Si(OR)_{4-x}(OH)_x$  or oligomeric species (which have more Si-O-Si bonds), and vice versa in basic media.

• More branched (i.e., more highly condensed) networks are obtained under basic conditions and chain-like networks under acidic conditions, because reactions at central silicon atoms (i.e., atoms with two or three Si-O-Si bonds) are favored under acidic conditions, and reactions at terminal silicon atoms (i.e., atoms with only one Si-O-Si bond) under basic conditions.

• Organically substituted alkoxysilanes R'Si(OR)<sub>3</sub> react faster than the corresponding Si(OR)<sub>4</sub> under acidic conditions and slower under basic conditions.

• The acidity of a silanol group increases with the number of Si-O-Si bonds at the silicon atom. This is one of the reasons why the PZC changes with the degree of condensation.

An important feature of the chemistry of silicon alkoxides is that hydrolysis and condensation reactions compete during all steps of the sol–gel process. Figure 3 shows the reaction possibilities of a hypothetical trisiloxane intermediate as an example. It can react by either hydrolysis or condensation, and these reactions can occur on chemically different silicon atoms. Note that monomeric species ("cluster–monomer" aggregation leading to extension by one Si-O unit), oligomeric species ("cluster–cluster" aggregation), or even siliceous structures can be involved in the intermolecular condensation reactions ( $\equiv$ Si- in Figure 3d and 3e can be the silicon atom of a monomeric or oligomeric species or of a particle).

The situation is even more complex, since each possibility shown in Figure 3 has a different reaction rate, which is influenced to a different degree by the reaction parameters. The same is true for the different intermediates that are formed as hydrolysis and condensation reactions proceed; that is, each intermediate has its own set of kinetic parameters.



**Figure 3**: Reaction possibilities of a hypothetical linear trisiloxane intermediate during sol–gel processing of Si(OR)<sub>4</sub>: (a) further hydrolysis at terminal positions; (b) further hydrolysis at the central silicon atom; (c) intramolecular condensation leading to a cyclic trisiloxane; (d) intermolecular condensation of a monomeric or oligomeric silicate species at a terminal position; and (e) intermolecular condensation of a monomeric or oligomeric silicate species at the central position.

As indicated in Figure 3c, not only linear or branched structures can be formed, but closed structures as well. Many three-dimensional cage compounds, the so-called spherosilicates (Figure 4), with either closed or partially open cages, have been isolated. Such structures can also be substructures of the networks formed during sol–gel processing. Cage compounds (RSiO<sub>1.5</sub>)<sub>n</sub>, the so called POSS (polyhedral oligomeric silsesquioxanes), can be similarly obtained from R´Si(OR)<sub>3</sub>. Both POSS and spherosilicates are interesting building blocks for materials syntheses for their own [Pielichowski 2006].



**Figure 4**: Molecular structures of (XSiO<sub>1.5</sub>)<sub>n</sub> cages for n= 8, 10; X=R, H (POSS), OH, OR, O<sup>-</sup> (spherosilicates).

From what has been said, it is obvious that the systems are very complex and many different routes from the molecular precursor to the final silica gel are possible. The chemical parameters discussed in the following determine which route is taken. Because of this complexity, a detailed understanding (and awareness) of the parameters influencing the reaction rates and thus the structure evolution is necessary in order to tailor the texture and properties of sol–gel materials. The most important parameters influencing hydrolysis and condensation (and their relative rate) are:

- the kind of precursor(s),
- the pH (OH- or H+ catalysis), or other catalysts,
- the alkoxo group to water ratio (Rw) for alkoxide precursors,
- the kind of solvent,
- the presence of electrolytes,
- the temperature,
- the relative and absolute concentration of the components in the precursor
- mixtures, and other parameters.

#### 1.1.2. Precursors and pH effect

Different from water glass as a precursor, the Si-OR groups of silicon alkoxides must first be hydrolyzed before condensation reactions can take place. In addition to the inductive effects discussed above, the hydrolysis rates of alkoxysilanes are also influenced by steric factors. Any branching of the alkoxy group or increasing of the chain length lowers the hydrolysis rate of the alkoxysilanes. As discussed above, the reaction mechanisms for acid or base catalysis are very different. Furthermore, the reaction rates for hydrolysis and condensation of silicon alkoxides have different pH dependence (Figure 5).



**Figure 5**: Dependence of the relative rates of Si(OR)<sub>4</sub> hydrolysis and of condensation reactions on the pH.

The minimal reaction rate for hydrolysis is at pH 7, and for condensation at around pH 4.5. The latter corresponds to the PZC of silica. At pH < 5, hydrolysis is favored, and condensation is the rate-determining step. Many monomers or small oligomers with reactive Si-OH groups are simultaneously formed. In contrast, hydrolysis is the rate-determining step at pH > 5, and hydrolyzed species are immediately consumed because of the faster condensation. Catalysis by fluoride ions is similar to that of hydroxide ions (basic conditions). The pH is an especially important parameter to control the texture of gels from water glass solutions. At intermediate pH, the reaction rate of condensation is proportional to the concentration of the OH<sup>-</sup> ions (see Figure 2). At pH lower than about 2, the silicic acid species are positively charged, and according to the mechanism given in Figure 2, the reaction rate of the condensation is proportional to the concentration of the solutions contain mainly anionic species. For this reason, the rate of Si-O-Si cleavage or redissolution of particles is high at high pH (see Figure 5).

#### 1.1.3. Alkoxo Group/H<sub>2</sub>O Ratio (Rw)

The overall reaction for sol-gel processing of tetraalkoxysilanes implies that two equivalents of water (Rw=2) are needed to convert Si(OR)<sub>4</sub> to SiO<sub>2</sub>. Four equivalents of water (Rw=1) are needed for the complete hydrolysis of Si(OR)<sub>4</sub> if no condensation

would take place. Increasing the water proportion (i.e., lowering Rw) generally favors the formation of silanol groups over Si-O-Si groups. The Rw, together with the kind of catalyst, thus strongly influences the properties of the silica gels.

#### 1.1.4. Solvent and Electrolytes

A solvent may be necessary to homogenize the reaction mixture of alkoxidebased systems, especially at the beginning of the reaction. Polarity, dipole moment, viscosity, and protic or nonprotic behavior of the solvent influence the reaction rates and thus the structure of the final sol–gel material.

Increasing the electrolyte concentration in a colloidal dispersion compresses the electrical double layer around the particles, because the number of charges required to balance the surface charge is now available in a smaller volume surrounding the particle. The colloid will eventually coagulate because the attractive force between the particles is unchanged, while the repulsive barrier is reduced.

Therefore, the presence of electrolytes (salts) has a strong influence on the gelation behavior. To render sol–gel processes reproducible, special care has to be taken (especially in alkoxide-based systems) not to introduce unwanted salt contaminations in the system, for example, through the water used for hydrolysis of alkoxides. An oftenneglected source of ionic species is the counterions of the acids or bases needed for catalysis. The reason why ammonia is mostly used as a base is that it is not ionic. Acids are more problematic, because anionic species (the counterions) are inevitably introduced and influence the reaction rates and the gelation behavior.

#### **1.2 Metal Oxide-Based Materials**

Any metal oxide can, in principle, be prepared by sol-gel processing. There are two important differences between silicon (as a semimetal) and typical main group or transition metals that are highly relevant for sol-gel chemistry [Schubert 2003]:

• Metals are more electropositive (Lewis acidic) than silicon and therefore more susceptible to a nucleophilic attack.

• The preferred coordination number of silicon is 4, and is thus equal to its valence (+IV). For metals, especially transition metals, on the other hand, the preferred coordination number is higher than their valence. The increase of the coordination

number beyond the valence is reached by interaction with any nucleophilic (Lewis basic) entity in the system, as will be discussed in more detail below.

As in silicate sol–gel processes, inorganic or metal–organic (alkoxide) precursors can be used. Many metal salts are hydrolytically unstable; that is, they form oxide/hydroxide precipitates from aqueous solutions upon pH changes. This is due to the fact that water molecules coordinated to metal ions are more acidic than those in the noncoordinated state due to charge transfer from the oxygen to the metal atom. The series of equilibria shown in Figure 6 is more easily shifted to the right than in water itself when the pH is increased (i.e., if a base is added).



Figure 6: Series of equilibria.

Condensation reactions, that is, formation of M-O-M links with concomitant cleavage of  $H_2O$ , require the presence of M-OH units (as for silica, Figures 1 and 2). This means that the equilibria in Figure 6 must be shifted in the M-OH regime, which depends on the valence of the metal and the pH. This is schematically shown in Figure 7. There are three possibilities to shift the equilibria in the M-OH regime:



**Figure 7**: Charge (Z) versus pH diagram indicating the domains of aquo, hydroxo, and oxo species. Note that the lines only roughly indicate transitions between the corresponding domains.

• Raising the pH corresponds to moving from left to right in Figure 7 for a given valence (Z). For example, when aluminum salts are dissolved in water, the

hydrated cation  $[Al(H_2O)_6]^{3+}$  exists only below pH 3. As the pH is increased, the water ligands are deprotonated, and the ions  $[Al(OH)_x(H_2O)_{6-x}]^{(3-x)+}$  are formed. Mononuclear species with x =0–4 are stable only in very dilute solutions; at higher concentrations, polynuclear species are formed by condensation reactions, that is, by formation of Al-O-Al links. Alternatively, the solution can simply be aged at elevated temperatures. A higher temperature promotes dissociation of protons from the hydrated metal ions.

- Solutions of metallate ions, such as titanates, vanadates, niobates, tantalates, or tungstates, form gels when acidified (right to left in Figure 7 for a given valence).
- Solutions of oxide species with the metal in high oxidation states can be reduced to give gels (top-down in Figure 7 at a given pH); one of the best-known examples is the formation of MnO<sub>2</sub> gels from MnO<sub>4</sub><sup>-</sup>.

As in the case of silica-based sol–gel processes, M-OH groups can also be created by hydrolysis of M-OR groups, that is, by addition of water to metal alkoxides. As outlined above, metal alkoxides are stronger Lewis acids than silicon alkoxides, and the formation of higher coordinated species is easier. Nucleophilic attack at the metal is thus facilitated, and the hydrolysis rates are strongly increased.

#### **1.3 Sol–Gel Transition**

#### 1.3.1. Hydrolytic Sol-Gel Processes

The crystalline state of a solid compound is thermodynamically more favorable than the amorphous state. In order that crystallization can occur, however, (crystalline) nuclei must be formed and growth of the nuclei must be possible. If either nucleation or crystal growth is inhibited under a given set of experimental conditions, amorphous materials are formed, which include glass-like materials and gels. The formation of amorphous networks (i.e., networks without a three-dimensional order) is particularly favored if there are many degrees of freedom for the mutual arrangement of the building blocks.



Figure 8: Structural development of silica gels [Iler 1979].

This is the reason why silica-based materials form gels more easily than other oxides, and consequently the chemistry of silica gels is particularly well investigated. The following discussion of gelation is thus focused on silica, but is analogous for other materials (e.g. TiO<sub>2</sub>). In the initial stage of sol–gel reactions, small three-dimensional oligomeric particles are formed. Figure 8 schematically shows the structural development of silica gels from molecular precursors. Whether the initially formed primary (nano)particles aggregate once they have reached a certain size or continue to grow depends on the experimental conditions. Aggregation of the primary particles may lead to (larger) secondary particles (features at the descending branches in the left part of Figure 8). Whether the particles (with a polymeric or dense substructure) may remain suspended in solution (i.e., form a stable sol) or aggregate to form a three-dimensional network (i.e., a wet gel) again depends on the system and the experimental conditions. The basic chemical processes (hydrolysis and condensation), however, are the same. In nonsilicate systems, the network- forming (nano)particles may be crystalline or semicrystalline.

As the sol particles aggregate and condense, the viscosity of the sol gradually increases. The sol–gel transition (gel point) is reached when a continuous network is formed. Before the gel point has been reached, the colloidal dispersion behaves like a more or less viscous liquid. At the gel point, the viscosity increases sharply, and a form-stable, elastic gel body is obtained. From a practical point of view, the gel time ( $t_{gel}$  =time at which the gel point is reached after starting hydrolysis and condensation reactions) is determined by turning the reaction vessel upside down. Since all liquid is retained in the gel body, no liquid can flow out of the vessel. For the same reason, the volume of the gel in this stage is the same as that of the original precursor solution.

Typical  $t_{gel}$  values for Si(OEt)<sub>4</sub> are 92h with 0.05 mol of HCl or 107h with 0.05 mol of NH<sub>4</sub>OH as the catalyst. Without a catalyst, tgel would be about 1000h [Pope 1986]. The tgel is generally lowered by all parameters that increase the rate of condensation reactions, as discussed above. These parameters thus allow to deliberately influence the gel times.

A wet gel, by definition, consists of a continuous solid network, the pores of which contain a liquid phase. At the gel point, however, unbound oligomers of various sizes or even monomeric species are still dissolved or dispersed in the pore liquid. This is important for the aging of gels.

The simplest picture of gelation is that the particles grow by aggregation or condensation until they collide to give clusters of particles. (Note that in the models describing gelation, the term "cluster" is used equivalent to "particle" or "oligomeric species.") The clusters become bigger and bigger by repeated collisions. This process produces clusters of various sizes. In this picture, which is mathematically described by the percolation theory, the gel is formed when the last link between two giant clusters of particles is formed. This is called the "spanning cluster," that is, a cluster that reaches across the vessel that contains it. Note that the bond resulting in the formation of the spanning cluster is not different from the previously formed bonds; that is, gelation is not a special thermodynamic event.

An alternative description of gelation is given by kinetic growth models. These also explain the different microstructures upon changing the reaction conditions. Depending on the conditions, growth in silicate systems may occur predominantly by condensation of clusters with monomers or with other clusters. The rate of the condensation reactions may be diffusion or reaction limited. As has been discussed before, hydrolysis of silicon alkoxides is faster than condensation under acidic conditions. Since all species are hydrolyzed at an early stage of the reaction, they can condense to form small oligomeric species (clusters) with reactive Si-OH groups. Under these conditions, reactions at terminal silicon atoms are favored (see above). This results in polymer-like gels; that is, small clusters undergo condensation reactions with each other to give a polymer-like network with small pores. Monomer–cluster growth, on the other hand, requires a continuous source of monomers. Hydrolysis is the rate-determining step under basic conditions. The hydrolyzed species are immediately consumed by reaction with existing clusters because of the faster condensation reactions. Furthermore, the rate of hydrolytic cleavage of (terminal) Si-O-Si bonds is much higher than that under acidic conditions. This additionally ensures that a source of monomers is available.

Condensation of clusters among each other under these conditions is relatively unfavorable because this process requires inversion of one of the silicon atoms involved in the reaction. Reaction at central silicon atoms of an oligomer unit is favored under basic conditions (see above). The resulting network therefore has a particulate character with big particles and large pores (colloidal gels). The formation of larger particles, mainly in aqueous systems, is also favored by Ostwald ripening by which small particles dissolve and larger particles grow by condensation of the dissolved species. Solubility of a particle is inversely proportional to its radius. The solubility of nanoparticles (<5 nm) therefore is rather high. Growth stops when the difference in solubility between the smallest and the largest particles in the system becomes only a few ppm. Solubility depends on the given conditions (temperature, pH of the solution, etc.). At higher temperatures, larger particles are obtained because the solubility of silica is higher. Therefore, materials with a different structure will be obtained by working in solutions of different pH [Hüsing 1998].

#### **1.4 Silica Particles (SiO<sub>2</sub>) via Stöber Process**

The Stöber process is a sol-gel chemical process used to prepare silica (SiO<sub>2</sub>) particles [Stöber 1968] of controllable and uniform size [Bogush 1988] for applications in materials science. It was pioneering [Drašar 2016] when it was reported by Werner Stöber and his team in 1968, [Stöber 1968] and remains today the most widely used wet chemistry synthetic approach to silica nanoparticles [Drašar 2016]. It is an example of a sol-gel process wherein a molecular precursor (typically TEOS) is first reacted with water in an alcoholic solution, the resulting molecules then joining together to build

larger structures. The reaction produces silica particles with diameters ranging from 50 to 2000 nm, depending on conditions. The process has been actively researched since its discovery, including efforts to understand its kinetics and mechanism. A particle aggregation model was found to be a better fit for the experimental data [Bogush 1991] than the initially hypothesized LaMer model [LaMer 1950]. The newly acquired understanding has enabled researchers to exert a high degree of control over particle size and distribution and to fine-tune the physical properties of the resulting material in order to suit intended applications.

In 1999 a two-stage modification was reported [Boissière 1999], that allowed the controlled formation of silica particles with small holes [Boissière 2000]. The process is undertaken at low pH in the presence of a surface-active molecule. The hydrolysis step is completed with the formation of a microemulsion [Prouzet 2005] before adding sodium fluoride to start the condensation process. The non-ionic surfactant is burned away to produce empty pores, increasing the surface area and altering the surface characteristics of the resulting particles, allowing for much greater control over the physical properties of the material [Boissière 1999]. Development work has also been undertaken for larger pore structures such as macroporous monoliths [Cademartiri 2009], shell-core particles based on polystyrene [Ding 2004], cyclen [Masse 2009], or polyamines [Masse 2008], and carbon spheres [Liu 2011].

Silica produced using the Stöber process is an ideal material to serve as a model for studying colloid phenomena [Berg 2010] because of the monodispersity (uniformity) of its particle sizes [Boday 2015]. Nanoparticles prepared using the Stöber process have found applications including in the delivery of medications to within cellular structures [Prokop 2014] and in the preparation of biosensors [Ju 2011]. Porous silica Stöber materials have applications in catalysis [Ramirez 2003] and liquid chromatography [Kruk 1999] due to their high surface area and their uniform, tunable, and highly ordered pore structures. Highly effective thermal insulators known as aerogels can also be prepared using Stöber methods [Berg 2010], and Stöber techniques have been applied to prepare non-silica aerogel systems [Qiu 2015]. NASA has prepared silica aerogels with a Stöber-process approach for both the Mars Pathfinder and Stardust missions [Nixon 2012].

The Stöber process is a sol-gel approach to preparing monodisperse (uniform) spherical silica (SiO<sub>2</sub>) materials that was developed by a team led by Werner Stöber and reported in 1968 [Stöber 1968]. The process, an evolution and extension of research described in Gerhard Kolbe's 1956 Ph.D. dissertation [Kolbe 1956], was an innovative discovery that still has wide applications more than 50 years later [Drašar 2016]. Silica precursor TEOS is hydrolyzed in alcohol (typically methanol or ethanol) in the presence of ammonia as a catalyst [Stöber 1968].

$$Si(OEt)_4 + H_2O \rightarrow Si(OEt)_3OH + EtOH$$
 (1.7)

$$Si(OEt)_4 + 2H_2O \rightarrow Si(OEt)_2(OH)_2 + 2EtOH$$
(1.8)

The reaction produces ethanol and a mixture of ethoxysilanols (such as  $Si(OEt)_3OH$ ,  $Si(OEt)_2(OH)_2$ , and even  $Si(OH)_4$ ), which can then condense with either TEOS or another silanol with loss of alcohol or water [Van Blaaderen 1992] (see Figure 9).

$$2Si(OEt)_{3}OH \rightarrow (EtO)_{3}Si-O-Si-(OEt)_{3} + H_{2}O$$
(1.9)

$$Si(OEt)_3OH + Si(OEt)_4 \rightarrow (EtO)_3Si-O-Si-(OEt)_3 + EtOH$$
 (1.10)

$$Si(OEt)_{3}OH + Si(OEt)_{3}(OH)_{2} \rightarrow (EtO)_{3}Si-O-Si-(OEt)_{2}OH + H_{2}O$$
(1.11)



Figure 9: Sol-gel reactions of TEOS silica precursor.

Further hydrolysis of the ethoxy groups and subsequent condensation leads to crosslinking. It is a one-step process as the hydrolysis and condensation reactions occur together in a single reaction vessel [Stöber 1968].

The process affords macroscopic particles of granular silica with diameters ranging from 50 to 2000 nm; particle sizes are fairly uniform with the distribution determined by the choice of conditions such as reactant concentrations, catalysts, and temperature [Bogush 1988]. Larger particles are formed when the concentrations of water and ammonia are raised, but with a consequent broadening of the particle-size distribution [Van Helden 1981]. The initial concentration of TEOS is inversely proportional to the size of the resulting particles; thus, higher concentrations on average lead to smaller particles due to the greater number of nucleation sites, but with a greater spread of sizes. Particles with irregular shapes can result when the initial precursor concentration is too high [Van Helden 1981]. The process is temperature-dependent, with cooling (and hence slower reaction rates) leading to a monotonic increase in average particle size, but control over size distribution cannot be maintained at overly low temperatures [Bogush 1988].

#### 1.4.2. Two-step process

In 1999 Cédric Boissière and his team developed a two-step process whereby the hydrolysis at low pH (1-4) is completed before the condensation reaction is initiated by the addition of sodium fluoride (NaF) [Boissière 1999]. The two-step procedure includes the addition of a nonionic surfactant template to ultimately produce mesoporous silica particles [Boissière 2000]. The main advantage of sequencing the hydrolysis and condensation reactions is the ability to ensure complete homogeneity of the surfactant and the precursor TEOS mixture. Consequently, the diameter and shape of the product particles as well as the pore size are determined solely by the reaction kinetics and the quantity of sodium fluoride introduced; higher relative fluoride levels produces a greater number of nucleation sites and hence smaller particles [Boissière 1999]. Decoupling the hydrolysis and condensation process affords a level of product control that is substantially superior to that afforded by the one-step Stöber process, with particle size controlled nearly completely by the sodium fluoride-to-TEOS ratio [Boissière 1999].

The two-step Stöber process begins with a mixture of TEOS, water, alcohol, and a nonionic surfactant, to which hydrochloric acid is added to produce a microemulsion [Prouzet 2005]. This solution is allowed to stand until hydrolysis is complete, much like

in the one-step Stöber process but with the hydrochloric acid replacing the ammonia as catalyst. Sodium fluoride is added to the resulting homogeneous solution, initiating the condensation reaction by acting as nucleation seed [Boissière 1999]. The silica particles are collected by filtration and calcined to remove the nonionic surfactant template by combustion, resulting in the mesoporous silica product.

The selection of conditions for the process allows for control of pore sizes, particle diameter, and their distributions, as in the case of the one-step approach [Boissière 2000]. Porosity in the modified process is controllable through the introduction of a swelling agent, the choice of temperature, and the quantity of sodium fluoride catalyst added. A swelling agent (such as mesitylene) causes increases in volume and hence in pore size, often by solvent absorption, but is limited by the solubility of the agent in the system [Prouzet 2005]. Pore size varies directly with temperature [Boissière 1999], bound by the lower out of the surfactant cloud point and the boiling point of water. Sodium fluoride concentration produces direct but non-linear changes in porosity, with the effect decreasing as the added fluoride concentration tends to an upper limit [Boissière 2001].

#### **1.5 Titanium Dioxide (TiO<sub>2</sub>)**

Titanium dioxide (TiO<sub>2</sub>) is the most common oxide of titanium, a transition metal found in group IV of the periodic table, with atomic number 22. Titanium is the ninth most abundant element and the fourth most abundant metal (and the second transition metal after iron) in the Earth's crust (about 0.6 %). The most relevant mineral sources are rutile, ilmenite and leucoxene, containing varying amounts of titanium dioxide. The world's production of TiO<sub>2</sub> is over 4 million tons per year. The majority is used as white pigment, because of its opacity and high refraction index (2.5 - 2.7, according to the crystalline structure). TiO<sub>2</sub> can be found as pigment in paints, plastic, ceramics, paper, toothpastes and other cosmetics, pharmaceuticals and food (as E171 colouring agent). It is commonly a component of sunscreen formulations for its ability of blocking ultraviolet radiation [Carp 2004, Chen 2007].

 $TiO_2$  exists in several crystalline forms (11 have been identified), the most important at common temperatures and pressures being rutile, anatase and brookite. In these structures each  $Ti^{4+}$  cation is coordinated by six  $O^{2-}$  anions, and the phases differ by the distortion and assembly patterns of the  $[TiO_6]$  octahedra. In rutile each  $[TiO_6]$ 

octahedron is surrounded by ten octahedra, sharing an edge with two of them and a corner with the other eight, in a tetragonal crystalline system; in anatase each [TiO<sub>6</sub>] octahedron is surrounded by eight octahedra (four edge-sharing and four cornersharing), in a distorted tetragonal system, with longer Ti-Ti and shorter Ti-O distances; in brookite the octahedra share three edges in an orthorhombic system. These differences in the crystal lattice cause differences in mass density (4.26, 4.11 and 3.84 g/cm<sup>3</sup> for anatase, brookite and rutile, respectively) and electronic structure, e.g. the band gap energy. Rutile is the most thermodynamically stable phase at most temperatures and pressures, due to its linearity which allows relaxation of Ti-Ti bonds, while metastable anatase and brookite are kinetic products. Anatase is the most commonly produced phase at low temperatures, while brookite can be obtained as byproduct or in specific synthesis conditions. The conversion of anatase to rutile occurs at T > 600 °C and depends on factors like particle size and the presence of surface or lattice defects [Carp 2004, Chen 2007, Kumar 2014].

Titanium dioxide is characterized by large availability, low cost, chemical and mechanical stability, biological inertness, good electrical properties. Besides the use as pigment, it finds applications in gas sensing, biomaterials (in bone implants), anti-reflective, anti-corrosion or anti-fogging coatings, photochromics and electrochromics, dielectrics, photovoltaic cells, catalysis and photocatalysis (including self-cleaning surfaces).

As catalyst, TiO<sub>2</sub> is employed in particular for its redox ability, in reactions like the selective reduction of NO<sub>x</sub> to N<sub>2</sub>, the decomposition of volatile organic compounds (VOC), hydrogen production by water gas shift, Fischer-Tropsch synthesis, CO oxidation by O<sub>2</sub>, H<sub>2</sub>S oxidation to S and SO<sub>2</sub> reduction to S by CO [Carp 2004]. TiO<sub>2</sub> was also proposed as an acid heterogeneous catalyst, as anatase was shown to have a considerable density of Lewis acid sites that can work stably in water [Nakajima 2013 14]. TiO<sub>2</sub> is often used as catalyst support; the possibility of tailoring its surface and morphological properties (crystalline phase, exposed facets, particle size and shape, surface area, porosity) favours the obtainment of catalytic materials with the desired features, by functionalization and deposition of active species, such as metals or other metal oxides.

As a wide band gap semiconductor,  $TiO_2$  is the reference metal oxide in the research on photocatalysis. Heterogeneous photocatalysis refers to the process involving redox

reactions on the surface of a semiconductor by means of electrons and holes separated by the absorption of light. Several advantages, besides those mentioned above, justify the focus on TiO<sub>2</sub> in fundamental and applicative photocatalytic studies: chemical and electrochemical stability in a wide range of conditions, photostability, high photoreactivity (with photonic efficiency up to 10 %), high electron mobility, suitable redox potential of valence and conduction bands [Schneider 2014, Fujishima 2008]. The first hints on the reactivity of TiO<sub>2</sub> under sunlight have been recognized in the first half of the XX century, for example observing the degradation of the organic components of paints containing titania [Fujishima 2008].

Nonetheless, the interest on its photoresponsive properties started growing after the renowned paper published in 1972 by Honda and Fujishima, demonstrating water splitting to  $H_2$  and  $O_2$  on an illuminated rutile electrode [Fujishima 1972].

 $TiO_2$  has a band gap energy between the valence and conduction bands generally ranging from 3.0 eV (rutile) to 3.2 eV (anatase), with slightly higher values for amorphous samples and thin films, and values lower of about 0.2 eV reported for some nanosized samples (up to 5-10 nm) due to the quantum confinement effect. The valence band potential is positive enough to promote the O<sub>2</sub> evolution from water and the generation of the strongly oxidizing hydroxyl radical ('OH), while the conduction band potential is negative enough to allow water reduction to H<sub>2</sub> and O<sub>2</sub> reduction to superoxide radical  $(O_2^{-})$ , another important reactive oxygen species [Fujishima 2008]. The properties of TiO<sub>2</sub> are strictly dependent on both the crystalline form and the structure and morphology of the material; different nanostructures, e.g. nanoparticles, nanorods, nanotubes, nanosheets, hollow spheres, can be obtained using different synthesis methods and show peculiar behaviour with respect to the bulk oxide. The anatase polymorph has been commonly recognized as the most active in photocatalysis, mainly because of its higher electron mobility, lower dielectric constant, better band positions and more efficient surface interaction with oxygen species [Fujishima 2008]. Nevertheless, recent studies have provided contrasting data on the actual band potentials of anatase and rutile, and showed that rutile can be more efficient in reducing processes [Buchalska 2015, Scanlon 2012]. The most investigated commercial TiO<sub>2</sub> is known as "P25", a mixture of about 75% anatase and 25% rutile, usually taken as a standard reference for photocatalytic activity. Its outstanding activity is related to the charge transfer between the two phases, anyway a complete knowledge of the exact mechanism of their interplay is not yet achieved. Brookite and other TiO<sub>2</sub> polymorphs have received less attention, also because of the difficulty in obtaining them in pure form.

Amorphous titanium oxide is generally considered of very restricted photocatalytic activity, since the disordered structure hinders the transport of electron and holes, fostering their recombination [Ohtani 1997]. On the other hand, amorphous materials can present some favourable characteristics for a catalytic process, for instance large surface area, high surface hydroxylation and hydration, therefore a better adsorption of substrate molecules, easiness of preparation. Few reports of amorphous TiO<sub>2</sub> with interesting photocatalytic performances are indeed found in literature, for instance hydrated, defective or  $H_2O_2$ -modified amorphous TiO<sub>2</sub> samples, prepared by sol-gel or precipitation method [Zhang 2007, Carrus 2016, Fan 2015, Zywitzki 2017, Seo 2017].

#### 1.5.1. Sol–Gel Synthesis of TiO<sub>2</sub>

Depending on the titanium metal precursor type, two types of sol–gel process canbe identified to produce  $TiO_2$  semiconductors: (i) an alcohol-based process where the starting precursor is metal alkoxide and (ii) an aqueous-based process where the starting precursor is inorganic metal salt.

#### 1.5.2. Alcohol-Based Process

The important metal alkoxide precursors of  $TiO_2$  are  $Ti(OC_2H_5)$ ,  $Ti(OC_3H_7)_4$  and  $Ti(OC_4H_9)_4$ . In these alkoxides, there exists a metal–oxygen bond and due to large difference in electro-negativity between Ti and O, the bond becomes highly polarand extremely reactive. Hence by addition of water, simultaneous hydrolysis and condensation reactions proceed ultimately leading to the formation of a gel [Schubert 2005].

#### 1.5.3. Aqueous-Based Process

The important precursors for the aqueous-based process are TiOSO<sub>4</sub> [Periyat 2007] and TiCl<sub>4</sub> [Baiju 2007]. Aqueous-based sol–gel preparation can also be done using a hydrolysis and condensation method. The slow controlled nucleation and growth of crystals at an elevated temperature form the particles that can also be used [Periyat 2015]. Steps involved in the aqueous-based sol–gel process are precipitation and peptisation. Precipitation involves the hydrolysis of the inorganic metal salt, which hydrolyses rapidly to get a gelatinous precipitate by the addition of base, followed by

washing to remove excess electrolyte. Peptisation is generally the process of redispersing a colloid which will prevent coagulation [Schubert 2005]. Peptisation actually refers to a direct disintegration of substance into particles of colloid size by an added agent known as peptising agent [Varma 1994]. It is very difficult to peptise a colloid that has been fallen into a primary potential minimum.

#### 1.5.4. Role of organic ligands

Frequently, the reactivity of metal alkoxides towards water needs to be controlled, in order to achieve cross-linking between clusters and gelation instead of precipitation. This is the case of titanium alkoxides, Ti(OR)<sub>4</sub>, which show a very high reactivity toward the hydrolysis and condensation reactions due to the high polarity of Ti-O bond, generating a positive partial charge on the Ti atom and making it very susceptible to nucleophilic attack. Chemical additives can be added during the synthesis procedure with the aim to moderate the reaction rate of the alkoxide. Complexing organic ligands (CL) are commonly used, in particular bidentate ligands able to form strong bridging or chelating coordination bonds with titanium. Widely studied examples are  $\beta$ -diketones, such as acetylacetone, and carboxylic acids, such as acetic or citric acid [Brinker 1990, Danks 2016, Livage 1988, Leaustic 1989, Doeuff 1987].

Metal alkoxides are Lewis acids, able to interact with compounds having a lone electron pair to increase their coordination. Bidentate ligands can react with them through nucleophilic substitution or addition, with the subsequent increase of coordination number. The reaction can be schematically written as follows, if CL-H is the complexing ligand and CL its deprotonated form:

$$M(OR)_{n} + xCL - H \rightleftharpoons M(OR)_{n-x}(CL)_{x} + x ROH$$
(1.12)

The heteroleptic compounds formed are new precursors having a different reactivity than the unmodified alkoxides. Their stability is determined by the equilibrium constant of the formation reaction. Multidentate ligands are more strongly bonded than monodentate ligands because of the chelate effect, therefore the stability constant of the corresponding complexes is higher. As a result, multidentate ligands are less readily hydrolysed than the remaining OR groups upon sol-gel processing. Although a partial cleavage of the M-CL bond normally cannot be avoided due to the coordination equilibrium, a substantial fraction of the CL can be retained in the obtained gels.

The replacement of one or more OR groups by CL has several consequences for the solgel processing:

- the degree of cross-linking of the gel network is decreased, because of the smaller fraction of hydrolysable OR groups;
- the substitution with multidentate ligands lowers the connectivity of the molecular building blocks, thus favoring the formation of gels instead of crystalline precipitates;
- the polarity variation by the organic groups has probably a similar effect on the network structure as changing the polarity of the solvent, affecting the formation of hydrogen bonds, important in the network structure;
- the complexing ligands may stereochemically direct the hydrolysis and condensation reactions because inductive effects give the site trans to an organic group a different reactivity than the cis sites.

A first mechanism proposed to explain the sol stabilization, is based on the hypothesis that a kinetic control is exerted by the modifying chelating ligand on hydrolysis and polycondensation reactions of metal alkoxides. According to this mechanism, chelating ligands block the coordination sites of ions such as Ti<sup>4+</sup>, decreasing their rate of hydrolysis and condensation [Schubert 2005].

A quite different interpretation was suggested more recently by Kessler et al. [Kessler 2006, Kessler 2009]. They showed that the hydrolysis and polycondensation of titanium and zirconium alkoxides are actually facilitated by their chemical modification, that the reactions have thermodynamic rather than kinetic control, and their kinetics is not directly related with the sol-gel transition. The complexing ligands show high mobility and their exchange results favored in protic solvents. Moreover, they increase the charge distribution in the complexes. As a consequence, chelating ligands increase the rate of hydrolysis and polycondensation, producing oxo-alkoxy oligomeric species. They apparently serve as nuclei for the growth of larger aggregates that, once reached a certain size (2-5 nm) become phase separated. These nanoparticles are formed by oxo-clusters (core) containing ligands on the surface (shell), exhibiting a structure typical of micelles, so they are called by the authors "micelles templated by self-assembly of ligands". The stabilization of the sol is a consequence of the interfacial activity of these micelles. In conclusion, if there are enough favorable interactions between the primary particles (including oxygen bridges and hydrogen bonding) and between the ligands and the

solvent, and if hydrolysis is not too fast, the particles can aggregate, develop common surface and finally lead to the formation of a uniform gel [Kessler 2006, Kessler 2009].

The control of hydrolysis rate is very important when multi-component systems (mixed oxides) are prepared. In fact, the choice of molecular precursors with comparable hydrolysis rates plays a key role in obtaining homogeneous sols in which cross-linking is preferred to self-condensation.

Besides controlling the reactivity of the metal alkoxides and the network structure of the obtained gels, the bidentate ligands can also be used to introduce functional organic groups into gels by means of appropriately substituted derivatives.

For this reason, in this PhD work we used an amorphous sol-gel titania complexed with a bidentate ligand such as acetylacetone, in order to improve the catalytic effect of titania.

# 1.6 Inorganic–Organic Hybrid Materials

The core of the present PhD project is the synthesis of hybrid materials based on electrospun polymer and silica and/or titanium oxide. Here the term "hybrid" indicates, as frequently occurs, the organic-inorganic composition, in this case an organic compound linked by chemical bonds to a metal oxide matrix. Hybrid organic-inorganic materials can be broadly defined as nanocomposites with organic and inorganic components which are intimately mixed [Sanchez 2005.]. As happens in other classes of composites, binding together components with completely different nature and features results in materials whose properties are not merely the sum of the properties of the single phases; indeed, new emerging properties appear, which cannot always be simply predicted and need careful investigation to be understood and applied.

One of the major advances of sol-gel processing is the possibility of synthesizing inorganic-organic hybrid materials, where organic and inorganic building blocks are combined. Sol-gel processing is a very suitable way to make such materials due to the mild processing conditions. The high temperature synthesis route to ceramic materials, for example, does not allow the incorporation of thermally labile organic moieties [Kickelbick 2007].

There are a wide range of possibilities to vary the composition and structure, and thus the properties of hybrid materials:

- chemical composition of the organic and inorganic moieties,
- ratio of the inorganic to organic components,
- kind of interaction between organic and inorganic moieties,

• structure of the building blocks, and distribution of the building blocks (random, blocklike, etc.).

Two different approaches can be used for the incorporation of organic groups into an inorganic network by sol–gel processing, namely, embedding of organic molecules into gels without chemical bonding (class I hybrid materials) and incorporation of organic groups through covalent bonding to the gel network (class II hybrid materials).

Embedding of organic molecules is achieved by dissolving them in the precursor solution. The gel matrix is formed around them and traps them, and the organic and inorganic entities interact only weakly with each other. A variety of organic or organometallic molecules can be employed, such as dyes, catalytically active metal complexes, sensor compounds, or even biomolecules or small particles. If sol–gel processing of alkoxides is performed in the solution of an organic polymer, the inorganic network (formed by sol–gel processing) and the organic network interpenetrate but are not bonded to each other. The presence of organic compounds may of course influence gelation because of polarity changes in the system. Very important sol–gel materials are obtained when functional or nonfunctional organic groups are covalently linked to oxide networks (class II materials).

Hybrid composites play an important role among advanced functional materials, as they offer virtually unlimited possibilities for tailoring shape and physicochemical properties, and facilitate miniaturization and integration, opening promising applications in many fields: optics, electronics, catalysis, sensors, membranes, functional and protective coatings, medicine, biotechnology, etc. [Sanchez, 2005]. Many kinds of inorganic-organic materials are currently commercially available.

# 2.0 Electrostatic spinning (Electrospinning)

With the rapid growth of nanoscience in recent years, nanofibers technology has been greatly accelerated to create nanoscale fibers from a broad range of polymeric materials. There are several approaches for generating fibers in a nanometer scale such as drawing, template synthesis, phase separation, self-assembly and electro static spinning (electrospinning). Although there are several methods for making fibers in a nanoscale range, none matches the popularity of the electrospinning technique due to its simplicity, cost effective and relatively high production rate [Tobing 2001].

While there are a number of different processing techniques that can be used for fabrication of nanofibers materials and composites, an additional unique synthetic method, electrostatic spinning (electrospinning), has received much attention lately. This process was patented by Antonin Formhals in 1934 [Formhals 1934] and has recently become an attractive method for the preparation of polymeric and composite nanofibers [Jeong 2010]. Electrospinning is a novel process for forming superfine fibers with diameters ranging from 10 µm down to 5 nm by forcing a polymer melt or solution through a spinneret with an electric field. It is currently the most widely used method for the production of polymeric nanofibers, due to its simplicity, cost effective, and suitability to yield very long fibers from various polymers. It can be simply carried out by applying a high voltage (several thousand volts/cm) to a capillary filled with polymer fluid (solution or melt), which is ejected out toward a counter electrode serving as the collector. The liquid jet undergoes a whipping process and splaying occurs in a region where the repulsive force from the electric charges carried by the jet becomes larger than its cohesive force. Splaying and solvent evaporation, together with a large elongation (because of the acceleration of the polymer jet by the electric force) are responsible for formation of the nanometer-sized polymeric fibers [Wang 2006].

Recently, electrospun fibers have attracted great attention due to their potential applications in many fields. To date, a variety of synthetic and natural polymers have been electrospun [Sell 2010, Rogina 2014], some important applications for these nanofibers include, but are not limited to nanocomposites [Jovanović 2004], fine filtration [Adams 2005], nanofibrous membrane for high performance batteries [Al Rai 2021], protective clothing [Baji 2020], scaffolds in tissue engineering [Ge 2007], drug delivery [Liu 2019] and wound healing [Rieger 2013].

#### **2.1 Electrospinning Process**

The apparatus used for electrospinning consists of a high voltage power supply with positive or negative polarity, a needle spinneret which is connected to the syringe with a polymer reservoir and a conducting flat plate or rotating drum which acting as a ground collector (see Figure 10). The polymer solution or molt is held by its surface tension in the form of a droplet at the needle tip (spinneret). When an electric potential is applied between the needle of syringe and collector, then increasing the voltage, charge is induced on the fluid surface and the pendant droplet of the polymer solution at the needle tip is deformed into a conical shape (Taylor cone). This occurs at the equilibrium of the electric forces and surface tension of the polymer solution or molt. When the intensity of the electrical fields surpasses a critical value, the electrostatic force will increase the electrostatic forces will overcome the surface tension of the polymer solution and consequently, a fine charged jet is ejected from the apex of the cone. Meanwhile, the solvent starts immediately to evaporate and finally the jet solidifies into fibers deposited on the collector plate.

In general, there are three main stages in the electrospinning of jet. The first one is the formation of Taylor cone in a fluid drop at the needle tip of the syringe. Then, a linear jet emerges from the bottom of the cone and moves towards the ground collector (stable region). After a few millimetres at most, a bending instability of the electrospun jet is observed due to the high electrostatic forces on the surface of the jet [Wang 2006].


#### Figure 10: Electrospinning apparatus

Bending instability is the region where the jet bends due to the high electrostatic forces on the surface of the jet at the tip of Taylor cone. When the pendent droplet at the needle tip is electrically charged by applying an electric field between the droplet and a ground plate, the droplet acquires a stable shape only if the electric field is not too high. This stable shape occurs only at the equilibrium between electric forces and surface tension of the droplet. Further increase of the electrical potential leads to distortion of this shape, and the droplet acquires a conical shape referred to as Taylor cone, having half of angle of 49.3°. Thus, Taylor cone refers to the cone observed in electrospinning from which a jet of charged particles emanates above a threshold voltage. The charged jet of the polymer is stretched and travels for a certain distance towards the ground electrode, then a bending (whipping) instability occurs and the jet transformed into superfine fibers. There are three different types of instabilities, like the so-called Rayleigh (Varicose) instability, in which the jet breaks into micron-sized droplets. However, another mode of instability is the axisymmetric conduction instability, in which the jet resulted in a bead structure. The bending (whipping) instability is the important one in the process, which is responsible to elongate the jet and forming the nanofibers. Bending instability of the charged jet occurs due to mutual repulsive forces between the electric charges transported by the jet. It can be defined as the region where the jet bends and stretching due to the high electrostatic forces on the surface of the jet. Bending instability was described by Sir Geoffrey Ingram Taylor in 1969 [Taylor 1969]. Recently, the mechanics of the whipping jet have been analyzed by studying the instability of an electrically driven jet with increasing field strength [Wang 2006].

#### 2.1.1. Parameters affecting electrospinning process

The electrospinning process is solely governed by many parameters, classified broadly into solution parameters, process parameters, and ambient parameters. Solution parameters include viscosity, conductivity, molecular weight, and surface tension and process parameters include applied electric field, tip to collector distance and feeding or flow rate. Each of these parameters significantly affect the fibers morphology obtained as a result of electrospinning, and by proper manipulation of these parameters we can get nanofibers of desired morphology and diameters (Chong et al., 2007). In addition to these variables, ambient parameters encompass the humidity and temperature of the surroundings which play a significant role in determining the morphology and diameter

of electrospun nanofibers (Li and Xia, 2004). In Table 1.0 are shown various parameters and their effects on fiber morphology.

Therefore, parameters that affect the electrospinning process and the fibers proprieties are divided in three main groups:

- solution parameters
- instrumental parameters
- ambient parameters

### 2.1.1.1. Solution Parameters

#### Concentration, Viscosity and Molecular Weight

It has been found out that the concentration of the solution needs to vary within a specific range in order to obtain acceptable results. Whenever the concentration is lower than a minimum value, the resulting electrospun material shows a mix of fibers and beads, while when it exceeds the maximum value, then it is impossible to maintain a constant flow at the tip of the needle. Hence, there is an optimal concentration within this range that allows to obtain the desired quantity and dimensions of fibers [Bhardwaj 2010, Zeng 2003]. Beads and beaded fibers are less likely to be formed for the more viscous solutions. The diameter of the beads becomes bigger and the average distance between beads on the fibers longer as the viscosity increases. Meanwhile, the shape of the beads gradually changes from spherical to spindle-like [Haghi 2007].

The solution viscosity has been strongly related to the concentration of the solution. An increase in solution viscosity or concentration gives rise to a large and more uniform fiber diameter. In electrospinning, the viscosity of a solution plays an important role in determining the range of concentrations from which continuous fibers can be obtained. For the solution of low viscosities, surface tension is the dominant factor and just beads or beaded fibers are formed while above critical concentration, a continuous fibrous structure is obtained, and its morphology is affected by the concentration of the solution [Zeng 2003].

The molecular weight of the polymer has a significant effect on the rheological and electrical properties, as viscosity, surface tension, conductivity and dielectric strength. It has been observed that a too low molecular weight solution tends to form beads rather

than fibers and a high molecular weight solution gives fibers with large average diameter.

The molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. Chain entanglement plays an important role in the processing of electrospinning [Nasouri, 2015, Kuchi, 2018].

#### Surface Tension and Conductivity

The surface tension basically depends on the type of solvent, reducing the surface tension it's possible to obtain beads free fibers and work at lower electrical fields.

As regard conductivity, ions play an essential role in fibers formation, determining their dimensions. In fact, to the increase of the electrical conductivity, corresponds a significative accretion of the electrospun fiber diameter. On the contrary, if the conductivity is inadequate, the electric force doesn't allow the jet formation. In this situation, salt ions are added to the solution to increase the conductivity and control the fiber dimension [Mit-uppatham, 2004].

#### 2.1.1.2. Instrumental Parameters

#### Voltage, Tip to Collector Distance and Flow Rate

The applied voltage is critical in electrospinning. The high voltage induces charges on the solution which are necessary in initiating electrospinning as the surface tension is overcome by the electrostatic forces in the solution. The applied voltage has a large effect on both nanofiber morphology and diameter. In most cases, a higher applied voltage leads to greater stretching of the polymer jet due to the greater columbic forces and stronger electric field, which results in thinner fiber diameter. However, lower voltages result in a decrease in fiber diameter due to the reduced acceleration of the jet and weaker electric field, which increases the time of flight of the jet allowing for more fiber stretching. In order to obtain thinner fibers, voltages closer to the critical voltage would be advantageous [Newsome 2014, Sill 2008].

The distance between the tip and the collector controls the fibers diameter and morphology. A minimum distance is required to give the fibers sufficient time to dry before reaching the collector, otherwise with too close or too far distances, beads have been observed. The effect of the tip and collector distance on the fibers morphology is not as significant as other parameters; nevertheless, an optimum distance between the tip and collector which favors the evaporation of a solvent from nanofibers is still required [Bhardwaj 2010].

The flow rate determines how much of the electrospinning solution is available at the tip of the spinneret for fiber formation. For a given voltage, there is a lower limit of flow rate for the Taylor cone to be stabilized. Increasing the flow rate above this increases fiber diameter because there is a greater volume of solution to be drawn from the spinneret tip [Sill 2008.]

## 2.1.1.3 Ambient parameters

## **Relative humidity and Temperature**

Relative humidity of the electrospinning environment influences the rate of evaporation of the solvent in the electrospinning jet. The range of relative humidity (0-55%) has a little effect on the overall morphology or average nanofiber diameter, some bead formation was observed at a RH above 50%. This effect has previously been observed in electrospinning of pure PVP nanofibers [De Vrieze, 2009].

At increased relative humidity with higher ambient water levels, PVP nanofiber diameter often decreases because the fluid PVP jet has a decreased solvent evaporation rate, allowing the charged jet more time to continue to elongate during electrospinning [Newsome 2014]. At the same time, the charge per unit area decreases as the surface area increases. Therefore, if the relative humidity is too high, jet instability is developed, and beaded nanofibers are formed as the surface tension forces in the jet overcome the forces promoting jet elongation. Thus, all electrospun samples are produced using ambient conditions where RH remains at, or below 50%.

As regard the temperature effect, it has been observed that with an increase in temperature, there is a production of fibers with a decreased diameter, and this decline has been attributed to the decrease in the viscosity of the polymer solution at increased temperature [Yang 2017].

 Table 1.0 Electrospinning parameters (solution, processing and ambient) and their effects on fiber morphology.

Parameters	Effect on fiber morphology
Solution Parameters	

Viscosity	Low-beads generation, high-increase in fiber diameter, disappearance					
	of beads					
Polymer concentration	Increase in fiber diameter with increase of concentration					
Molecular weight of	Reduction in the number of beads and droplets with increase of					
polymer	molecular weight					
Conductivity	Decrease in fiber diameter with increase in conductivity					
Surface tension	No conclusive link with fiber morphology, high surface tension					
	results in instability of jets					
Processing Parameters						
Applied Voltage	Decrease in fiber diameter with increase in voltage.					
Distance between tip and	Generation of beads with too small and too large distance, minimum					
collector	distance required for uniform fibers					
Feed rate/Flow rate	Decrease in fiber diameter with decrease in flow rate, generation of					
	beads with too high flow rate					
Ambient Parameters						
Humidity	High humidity results in circular pores on the fibers					
Temperature	Increase in temperature results in decrease in fiber diameter.					

## 2.1.2. Different morphology of nanofibers

Electrospinning provides a possibility to produce nanofibers with different structures and morphologies by varying the processing parameters. A number of methods have been employed in different contexts to fabricate polymeric nanofibers with different morphologies, namely, beaded, ribbon, porous, smooth and core-shell nanofibers [Koombhongse 2001]. The morphology of the electrospun nanofiber as well as fibers diameter can be changed by varying the electrospinning parameters to fit desired applications.

## 2.2 Properties and potential applications of electrospun fibers

Polymeric electrospun nanofibers and their composites materials exhibit many unique properties that distinguish them from the other conventional fibers. They possess a huge surface to volume ratio, low density, high porosity, and nano pores with highly interconnected internal structure [Huang 2003]. One of the most important property of the nanofibers is the superior mechanical behavior that nano-sized materials possess as compared to bulk materials. The superior mechanical properties of the electrospun nanofibers (such as higher elastic modulus and strength) arise from the decrease in diameter and the higher molecular orientation of the polymer molecules. The molecular orientation is produced by the stretching of the polymer jet during Electrospinning

[Najem 2014]. The mechanical properties of single nanofiber as well as nanofibrous scaffolds are extremely essential issue in several applications which can be improved by crosslinking of the nanofiber mats [Newsome 2014, Sethi 2008]. To improve the deficiency of the mechanical properties, a good selection of the materials should be taken into the consideration when fabricating fiber scaffolds. Furthermore, the mechanical properties can be manipulated through varying solution composition (blending) and altering the processing parameters. Furthermore, the special properties of the electrospun nanofibers make them suitable for a wide variety of applications including, protective clothing, sensors, filter media, drug delivery, tissue engineering, nanoelectronics, wound dressing, energy & environmental applications [Huang 2003].

## 2.3. Fiber nanocomposites

Polymer nanocomposites are the result of combination between polymers and organic or inorganic fillers at the nanometer scale. The filler can be one-dimensional (e.g., nanotubes and fibers), two-dimensional (e.g., clay), or three- dimensional (e.g., spherical particles). The development of nanocomposite materials with improved properties has dominated the field of material science. Recently, much work has been focused on the construction of nanocomposite materials due to the structural enhancements in physical and mechanical properties for these systems [Sanchez 2011]. The physical and mechanical enhancements result from the interaction between filler components and matrix (e.g., hydrogen bonds) at the nanometer scale. This interaction enables them to act as molecular bridges in the polymer matrix [Demir 2002].

However, the properties of these nanocomposite materials are highly dependent on how well the filler are dispersed within the polymer matrix. Achieving a uniform dispersion of the filler by conventional mixing methods is difficult as the high surface energy of the nano filler makes them very easily agglomerate. Among these methods, one of the most desirable processes for nanocomposites fabrication is electrospinning technique. It has been used to fabricate hybrid nanocomposites (organic/inorganic) nanofibers with a high dispersion of the nano fillers inside the fiber matrix [ Bhardwaj 2010, Ghobadi 2015]. Moreover, the unique combination of high specific surface area, flexibility and superior directional strength makes nanofibers nanocomposites promising materials for wide applications [Huang 2003].

# 3.0 State of art and objectives

## 3.1 Electrospun composites for acoustic applications: PVP/SiO<sub>2</sub>Np

Noise pollution is a remarkable problem in modern society and can constitute a real risk to the human health [Barber 1992, Crocker 2007, Engel 2014, Goines 2007]. Nowadays, reducing the noise level generated by engines has become an important challenge as regard the production of suitable soundproofing materials to reduce the damages induced by a continuous exposition to vibrations.

For this reason, the production of insulating materials for noise/sound control has increased as a result of technological changes and product requirements in many areas, including aircraft and spacecraft, ground and marine transportation vehicles, buildings, and manufacturing facilities [Crocker 2007, Mahashabde 2011, Zhao 2015, Harris 1991, Locke 2007]. These materials include fibers, foams, cavities, composites, and other solid and liquid structures of various types and shapes. It is reported that the absorption of sounds at various levels and frequencies is difficult using exciting technologies. Although significant progress has been made during the past few decades to improve the efficiency of sound absorption and weight reduction, the problems have not been addressed yet for higher sound absorption and cost-effective methods [Khan 2012].

Aircraft cabin comfort is an important design aspect for any aircraft manufacturer. The entire travel experience for passengers and aircrew on-board an aircraft is highly determined by the comfort, efficiency and level or diversity of services available in the cabin. The overall aim of any innovative approach adopted by aircraft manufacturers is to offer travelers the quietest, most comfortable and attractive cabin environment possible. Although all aircraft manufacturers are constantly improving their cabin noise comfort standards, it is expected that new vehicle cabin designs will integrate contemporary technologically advanced concepts, optimized for low fabrication and integration costs, as well as low weight while providing an enjoyable travel environment. In particular, they are interested in low-weight materials, which may help reduce fuel consumption and achieve lower noise levels.

Noise mitigation involves a set of strategies to reduce unwanted noise inside aircraft. It is known that any material that allows air to pass through it will act as a sound absorber/barrier. The friction of sound energy moving through the absorber reduces sound by transferring it into heat energy [Crocker 1997, Westre 2007]. Thicker absorbers usually offer greater resistance to air molecules because of the surface areas, so they are more efficient in absorbing sound molecules into heat. However, thicker absorbers will increase the overall weight of the aircraft and reduce fuel efficiency. Today, most noise absorbers that are used to control the aircraft's interior noise are porous membrane, cavity, perforated panel, and composite absorbers in the form of open- and closed-cell foams, fiberglass, cloth, mineral wool, acoustic ceiling tiles, and wood fibers. Most of these materials used in aviation are flame resistant and are approved by the Federal Aviation Administration (FAA) [Eatwell 2007].

Porous absorbers with open-pore structures include all porous and filamentary materials, such as mineral wool, fiberboard, fabrics, fleece, carpets, cotton, and special acoustic plaster. These may be effective for high frequencies with short wavelengths [Crocker 1997]. Porous materials are characterized by the fact that their surfaces allow sound waves to enter the materials through a multitude of small holes or openings. When a porous material is exposed to incident sound waves, the air molecules within the pores of the material are forced to vibrate and, in doing so, lose some of their original energy. This is because part of the energy of the air molecules is converted into heat due to thermal and viscous losses at the walls of the interior pores and tunnels within the material [Arenas 2010].

Porous sound absorbing materials are grouped in three categories: cellular, fibrous and granular; their typical microscopic arrangements and some of the physical models used to describe their absorbing mechanisms are represented in Figure 11.



Figure 11: The three main types of porous absorbing materials [Arenas 2010]

Most of the porous sound-absorbing materials commercially available are fibrous. Fibrous materials are composed of a set of continuous filaments that trap air between them. They are produced in rolls or in slabs with different thermal, acoustical, and mechanical properties. Fibers can be classified as natural or synthetic; natural fibers can be vegetable, animal or mineral. Synthetic fibers can be cellulose, mineral or polymer. Synthetic fibrous materials made from minerals and polymers are used mostly for sound absorption and thermal isolation. However, since they are made from high-temperature extrusion and industrial processes based on synthetic chemicals, often from petrochemical sources, their carbon footprints are quite significant.

An important microscopic parameter of a fiber is its diameter. The fiber diameter is directly related to the sound-absorbing characteristics of the material. In general, the

diameter of natural fibers tends to be larger than the diameter of synthetic fibers obtained by extrusion [Arenas 2010]

Innovative polymeric sound absorbers can be produced through electrospinning. Such technique can be used to produce micro/nanofibers ranging from 2 nm to several micrometers [Liu 2014, Huang 2003, Teo 2006, Rutledge 2007, Bhardwaj 2010, Agarwal 2013], in contrast to conventional synthetic fiber forming processes such as those used for high-speed spinning of nylon or polyester, where continuous fibers ranging from 10  $\mu$ m to 500  $\mu$ m are produced. Electrospinning has already been proposed in the field of sound absorption thanks to the small diameter of the electrospun fibers. [Avossa 2013].

The electrospun materials possess high specific surface area 100 to 10000 times greater than that of the traditional acoustical fibrous materials; as a consequence, noise absorption is expected to rise due to the higher friction between the air molecules of sound waves and the electrospun fibers and/or rubbing of the fibers [Khan 2012 9]. Several reports on the acoustical performance of electrospun polymer fibers well confirm the interest in the production of sound-absorbing materials through electrospinning [Khan 2012, Liu 2014, Bhardwaj 2010, Xiang 2011, Trematerra 2014].

It was determined that a high–surface area electrospun fibers in aircraft interior noisereduction systems has several advantages [Khan 2010]:

- many polymeric materials, including flame-resistant polymers, can be electrospun;
- the surface area of the nanofibers is 100 to 10,000 times more than conventional fibers, such as fiberglass, mineral fiber wool, open cell foam, acoustic ceiling tiles, and wood fibers;
- the noise absorption rate is expected to be exponentially more because of the interaction of air molecules of sound waves with the fiber surfaces;
- the overall weight of the materials used for the noise absorption will be less;
- the porosity of the nanofibers is much more compared with the fibers that are currently used in aircraft for noise reduction and insulations;
- physical and chemical characterizations of nanofibers are well known;
- nanofibers can enhance the physical properties of some of the materials;
- nanofibers can be electrospun on both composite and metal surfaces;

• Electrospinning is an economical and technologically mature method for bulk production.

### 3.1.1 Electrospun PVP/silica composite

#### 3.1.1.1 Property of PVP

Polyvinylpyrrolidone (PVP) was first invented by Walter Reppe of BASF in the late 1930s [Reppe 1941, Reppe 1943]. PVP is a special and unusual material because it can be soluble in both water and various organic solvents, such as alcohols, amines, acids, chlorinated hydrocarbons, amides and lactams, but PVP cannot be dissolved in the common esters, ethers, hydrocarbons and ketones. The reason is PVP has hydrophilic as well as hydrophobic functional groups, which can interact with different solvents. The polymerization of PVP is as shown in Figure 12 [Haaf 1985]. The molecular weights (Mw) of PVP are from 2500 to about 1000000 and can be polymerized in both aqueous solution and organic solvents. Low molecular weights of PVP can be polymerized in organic solvents due to the transfer reactions of the solvent and medium and high molecular weights of PVP can be obtained by aqueous solution using hydrogen peroxide initiator and organic initiator, respectively.



Figure 12: Polymerization of PVP[Haaf 1985].

PVP is one of the most commonly used biocompatible polymer in many applications, such as pharmaceuticals, cosmetics, beverages, adhesives, detergents, paints, electronics, and biological engineering materials, due to its specific advantages, like good adhesion property, excellent physiological compatibility, low chemical toxicity, high hydrophilicity, good complexation property, firm-forming ability, reasonable solubility in water and most organic solvents. The most important applications of PVP are listed in Figure 13 [Haaf 1985].



Figure 13: Applications of PVP [Haaf 1985]

Electrospun ultrafine PVP fibers were first introduced by Bognitzki et al [Bognitzki 2001] in 2001 and they successfully fabricated polyactide (PLA)/PVP blend fibers and removed one component from both fibers of symmetric blends or fibers containing either PLA or PVP as the major component. In 2004, Yang et al. [Yang 2004] first reported the pure electrospun PVP fibers and they examined the influence of solvents on the formation of PVP nanofibers with electrospinning and the solvents used were ethanol, dichloromethane (MC), N, N-dimethylformamide (DMF) and the mixture of ethanol/DMF or ethanol/MC [Yang 2004]. When using MC and DMF as solvent, the beaded PVP fibers are collected; when using ethanol as solvent, the PVP nanofibers are smooth even though the size distribution was broad (Figure 14 a, b, c). Also, the PVP nanofibers without beads can be obtained with ethanol/DMF solvent (50:50 w/w). Additionally, at the concentrations of 4, 6, and 8 wt %, the fiber diameters were 20, 35, and 50 nm, respectively (Figure 14 d). When the concentration of PVP solution reached higher than 10 wt %, the diameter increased drastically to 300 nm. Sun et al. [Sun 2006] also confirmed the trend of diameter of electrospun PVP nanofibers with the ethanol/DMF solvent through their experiments.



Figure 14: TEM images of PVP nanofibers electrospun from different solvent: (a) Ethanol;(b) MC; (c) DMF; (d) The changes in average diameter of PVP nanofiber electrospun from ethanol/DMF (50:50 w:w) with its concentration [Yang 2004].

## 3.1.1.2. Electrospun Silica composites

Silica is a material of particular interest due to the presence of silanol groups capable of a wide range of interactions with other species, such as proton donor or acceptor interactions, dipole– dipole interactions, induced dipole interactions, and interactions based on dispersion forces [Reich 2007]. Additionally, by incorporating inorganic fillers into organic fibers, nanocomposites combine the advantages of polymeric materials, such as light weight and flexibility, and inorganic materials, such as high mechanical strength, heat stability, and chemical stability [Chen 2009]. For example, silica/polymer nanocomposites are ideal for a wide variety of applications, including biomedical devices, membranes, sensors, and as extractive sorbents and chromatographic supports with high adsorption capacity [Keyur 2008, Shao 2002, Sawicka 2006]. Production of electrospun nanofibers containing silica (SiO<sub>2</sub>) has been accomplished by electrospinning a sol–gel solution, either with [Rho 2008, Wen 2010] or without [Choi 2003] a polymer, and by electrospinning a polymer solution blended with silica particles [Chen 2009, Kanehata 2007, Ji 2008a, Lim 2006, Sharma 2010]. In either case, the composite silica/polymer nanofibers can be calcined to selectively remove the polymer matrix [Kanehata 2007, Lim 2006].

Various polymers have been used to create electrospun silica nanoparticle/polymer nanofibers, including polyvinylalcohol (PVA) [Kanehata 2007], polyacrylonitrile (PAN) [Ji 2008a, Lim 2006], poly(methyl methacrylate) (PMMA) [Chen 2009], polyethylene oxide (PEO) [Lim 2006, Sharma 2010], polyacrylamide (PAM) [Lim 2006] and poly(vinylidene fluoride) (PVDF) [Kim 2011]. The most critical challenge with this approach is the homogenous nanoscale dispersion of the inorganic particles in the polymeric electrospinning solution and within the resulting composite nanofibers. Most often this means that the polymer and SiO<sub>2</sub> NP (silica nanoparticle) must share a common solvent for homogenous dispersion throughout the nanofiber composite. Therefore, most work with silica/polymer nanocomposites uses water-soluble or alcohol-soluble polymers, such as PVA or PEO [Chen 2009.] Using water- or alcohol-insoluble polymers such as PAN often results in a heterogeneous dispersion of particles in the electrospun nanofibers due to particle agglomeration and only very low levels of nanoparticles (1–5 wt %) can be dispersed successfully [Ji 2008(a,b)].

Nevertheless, using a water-soluble polymer in the electrospinning solution results in a water-soluble mat of nanofibers, which limits the application of silica-based nanocomposites fabricated with this approach. To obtain silica-based nanofibers which are insoluble in water, as-spun nanofibers require additional crosslinking to render the polymer insoluble or heating to selectively remove the soluble polymer itself. Therefore, using the water/ alcohol-soluble polymer PVP to create electrospun silica/polymer composite nanofibers would be ideal to promote the homogenous dispersion of silica nanoparticles at high concentrations in the electrospun nanocomposite, but these as-spun nanofibers would need to be crosslinked or heated to make them insoluble for

applications involving water. However, there are few reports of electrospun silica/PVP fibers which possess nanoscale diameters or are insoluble in water.

Recently, magnetic nanoparticles coated in silica have been electrospun with polyvinylpyrrolidone (PVP) [Andrady 2008]; using 0.64 mm silica coated magnetic nanoparticles (MNPs), the smallest obtained fibers were sub-micron (0.66 mm) with a relatively low final MNP concentration (7 wt %). In another case, fibers have been electrospun using an electrospinning solution which combined PVP, TEOS, and silica particles (0.8 mm) [Guo 2013]; however, the resulting fibers were micron-sized (2.5 mm) and the fibrous morphology was not maintained after calcination. In neither of these instances was the PVP thermally crosslinked for solvent resistance, which would limit their use in certain applications.

Herein, this PhD study report an ecofriendly electrospinning method to produce composite silica/polyvinylpyrrolidone (SiO<sub>2</sub>/PVP) nanofibers through the use of silica sol-gel nanoparticles dispersed in a polyvinylpyrrolidone alcohol solution. The purpose of this work was to produce the smallest diameter nanofibers possible while maintaining homogenous nanofiber morphology in order to obtain a promising acoustic absorber membrane for aircraft applications.

The structure and composition were studied Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FTIR) Spectroscopy and Thermo Gravimetric Analysis (TGA). The presence of SiO<sub>2</sub> dimensionally stabilize the mats upon thermal treatments that confers water resistance. The high fire resistance was evaluated by two Fire Test specified in Federal Aviation Regulation (FAR). The thermal conductivity was also determined through Differential Scanning Calorimetry (DSC). The acoustic behavior, studied through Impedance Tube method, shows excellent sound-absorption properties in the low and medium frequency range (where human sensitivity is high).

All the results have been discussed in detail in the Section 5.0.

# 3.2 Electrospun composites for environmental applications: PVP/SiO<sub>2</sub>Np/TiO<sub>2</sub>acac

With rapid economic development, environmental pollution has emerged as an increasingly serious problem. Water pollution is an area of particular concern because pollution rates currently exceed the self-purification abilities of natural water reservoirs. Approximately 0.7 million tons of dyes are generated annually across the globe, 10e15% of which are discharged into water bodies. Environmentally friendly techniques therefore need to be developed to address pollution issues.

## 3.2.1 Titanium dioxide (TiO<sub>2</sub>) electrospun composites

In recent years, many studies on pollution mitigation have been performed [Kongkhlang 2008, Im 2008, Wang 2014a, Lee 2014, Pant 2013]. These studies have shown that TiO<sub>2</sub> is potentially useful in a wide range of applications such as water remediation and air purification [Wang 2014b, Li 2014, Park 2004, Barakat 2008, Im 2007].

Titanium dioxide (TiO<sub>2</sub>) is a promising photocatalyst because of its high photocatalytic efficiency, chemical resistance, thermostability, mechanical robustness and low cost [Park 2013, Dong 2015, Hu 2007]. Furthermore, it is nontoxic, insoluble in water, and readily available.

TiO<sub>2</sub> nanoparticles are typically used as a suspended slurry [Pelaez 2012, Singh 2013]. Suspending nanoparticles by intense mixing can maximize light absorption and mass transfer, but requires an energy-intensive separation process such as membrane filtration for catalyst recovery. TiO<sub>2</sub> in general also exhibits low adsorption capacity toward priority organic pollutants, making it difficult to minimize reactive oxygen species (ROS) scavenging by background organic constituents in the bulk phase [Dong 2015, Singh 2013, He 2009, Zhang 2008]. Alternatively, TiO<sub>2</sub> can be immobilized onto a larger substrate to avoid the costly separation step. Using an appropriate support material can also offer an opportunity to adsorb and bring priority pollutants near photocatalytic sites to more efficiently utilize the short lived ROS (i.e., "bait-hook and destroy" strategy) [Brame 2014]. Several researchers have highlighted the benefits of coupling adsorption and photocatalytic degradation for effective removal of contaminants [Giannakis 2017, Huang 2013, Lee 2011, Jafry 2011]

Ideal substrate materials for photocatalyst immobilization should provide stable anchoring to prevent catalyst leaching, stability against ROS, and selective affinity toward target contaminants [Singh 2013].

Various materials have been considered as photocatalyst supports, including glass, silica, ceramic, polymers, activated carbon, alumina, zeolite, and stainless steel [Singh 2013, He 2009, Shan 2010, Carbonaro 2013, Lim 2016]. Biocompatible polymers, such as Polyvinylpyrrolidone (PVP), are promising substrates since they can interact with a wide variety of organic and inorganic compounds allowing an easy functionalization. During the electrospinning process PVP can be selectively attached on the plane, thereby reducing the surface tension and stabilizing the metal nanoparticles. Previous studies [Jang 2013, Cheng 2011, Nakataa 2012] have shown that the photocatalytic properties of various supporting materials can be improved by the addition of TiO<sub>2</sub> and electrospinning.

Electrospun polymeric networks are often employed as scaffolds or templates for the preparation of  $TiO_2$  ceramic fibers. Whereas, the potentials of fibrous composites like PVP- $TiO_2$ , where metal oxide is usually introduced in the form of sol-gel nanoparticles, are less widely investigated. Furthermore, several strategies have been used to enhance the photocatalytic ability of  $TiO_2$ , including the synthesis of novel hybrid  $TiO_2$  photocatalysts [Dhand 2015, Park 2002, Lee 2014].

Recently, a sol-gel synthesis route to obtain TiO<sub>2</sub>-based hybrid gels with specific features linked to their organic components has been developed [Sannino 2015]. In particular, TiO<sub>2</sub>-acetylacetonate (TiO<sub>2</sub>acac) amorphous xerogels have shown remarkable performance in the oxidative degradation of different aqueous organic pollutants (phenanthrene, 2,4-dichlorophenol, chlorophenoxy herbicides) without any need of light irradiation [Sannino 2015, Pirozzi 2020]. This uncommon catalytic activity makes these hybrid materials promising not only for water decontamination but also for the abatement of air pollutants and antimicrobial coatings. Moreover, the annealing of the hybrid gels produced anatase TiO<sub>2</sub>/carbon heterostructures active in photocatalytic hydrogen generation [Imparato 2020].

The author of this PhD thesis shows the successful electrospinning of PVP-based ternary composites including sol-gel SiO<sub>2</sub> nanoparticles (~160 nm size) and sol-gel hybrid TiO<sub>2</sub>acac microparticles (up to 90  $\mu$ m) along with thermal stabilization without any shrinkage. Challenges associated with electrospun mat shrinkage during thermal 50

treatment was studied and mitigated by using SiO<sub>2</sub> nanoparticles. The structural and morphological characterization of these mats, performed by FTIR, SEM, TEM, and EPR, shows the exceptional stabilization of the superoxide ion radical (O<sub>2</sub><sup>•-</sup>) the surface of composite electrospun mats. This shows that the functionality of hybrid TiO<sub>2</sub>acac microparticles remains intact even after prolonged thermal treatment (6 h). The formation and stabilization of superoxide ion radical (O<sub>2</sub><sup>•-</sup>) on the surface of composite mats makes them an interesting candidate for pollution control, and this feature of the composite mats was investigated using the methylene blue (MB) as a model pollutant [Parida 2021, Saleh 2020]. Interestingly, MB degradation test was carried out in dark to achieve satisfactory degradation.

All the results have been discussed in detail in the Section 5.0.

## 4.0 Experimental and Methods

## 4.1 Materials

Polyvinyl pyrrolidone (PVP) (MW:1,300,000 g mol<sup>-1</sup>), tetraethyl orthosilicate (TEOS), titanium(IV) n-butoxide ( $\geq$ 97%), acetylacetone (Hacac) ( $\geq$ 99%), 1-propanol (99.80%) and hydrochloric acid (37 wt%) were purchased from Sigma Aldrich (USA). Ammonium hydroxide solution (30–33% NH<sub>3</sub> in H<sub>2</sub>O) and ethanol (99.8% ACS) were purchased from Honeywell (USA).

## 4.2 Methods

### 4.2.1 Preparation of sol-gel silica nanoparticles

The silica nanoparticles (SiO<sub>2</sub>) were prepared through Stöber method using TEOS as a precursor (See Scheme 1.1). TEOS (7 mL) was added to a distilled ethanol (160 mL), water (13.4 mL) and ammonium hydroxide solution (5.38 mL) under stirring. Subsequently and after 1.5 h the particles were recovered by centrifugation (11500 rpm for 10 min) and washed three times with ethanol.



Scheme 1.1. A reaction scheme showing the synthesis of silica nanoparticles from TEOS; The first reaction includes the hydrolysis of TEOS to form Silicon tetrahydroxide, followed by second reaction which involves the condensation of the Silicon tetrahydroxide to produce silica nanoparticles with siloxane bridges (Si-O-Si).

### 4.2.2 Preparation of TiO<sub>2</sub>acac dry gel

The hybrid TiO<sub>2</sub> (TiO<sub>2</sub>acac) was prepared by a sol–gel route. A solution containing 10 mL of titanium(IV) n-butoxide, 1.20 mL of acetylacetone and 3.87 mL of 1-propanol was prepared and stirred for a few minutes at 50°C. A second solution containing 5.27 mL of distilled water, 7.0 mL of 1-propanol and one drop of HCl (37 wt%) was then prepared and mixed with the first one. The resulting molar ratio Ti:Hacac:1-propanol:H<sub>2</sub>O:HCl was 1:0.4:5:10:0.02. The solution obtained was vigorously stirred at 50°C for about 5 min, until the gelation occurred. A homogeneous yellow wet gel formed in a few minutes. The wet gel was left at room temperature for 24 h. After aging, the gel was dried under airflow at 30 °C. Finally, the xerogel was reduced to a powder and passed through a 90 µm sieve.

The general procedure followed for the synthesis of the  $TiO_2acac$  dry gel is illustrated in Scheme 1.2.



Scheme 1.2. Sol-gel procedure followed for the synthesis of the TiO<sub>2</sub>acac.

## 4.2.3. Electrospinning of PVP mats

The electrospinning apparatus used in this work, whose scheme, in a horizontal set up, shown in Figure 15, consists of a high voltage electric source, a syringe pump (Harvard Apparatus, Pump 11 Plus) holding a 12 mL plastic syringe (Nipro) with a needle (inner diameter of 0.6 mm and average length of 4 cm) acting as the cathode and a rigid copper foil collector acting as the anode.



Figure 15. Electrospinning apparatus. (a) Schematic horizontal setup; (b) Laboratory setup at Department of Chemical, Materials and Industrial Production Engineering of University of Naples – Federico II.

The electrospun solution was prepared by mixing 1 gr of PVP in 10 mL of ethanol. After 10 minutes of stirring, the final PVP concentration was 10 wt.%.

During the electrospinning process, a flow rate of 0.200 mL min<sup>-1</sup> was assured by the syringe pump. The solution was electrospun under an applied electrical potential of 20 kV over a fixed collection distance of 39 cm at room temperature  $(23 \pm 2 \,^{\circ}\text{C})$  and relative humidity (45 ± 10 %). To convey the electrospinning jet onto the collector, a copper string was placed at the bottom of the chamber at the same potential of the needle nozzle. The as-prepared electrospun non-woven mats were dried out at 80 °C for 60 min and stored in a desiccator.

### 4.2.4. Electrospinning of binary composite mats: PVP-SiO<sub>2</sub>

The electrospun solution was prepared by mixing two other ones:

- An ethanol solution (20 wt. %) of PVP (MW:  $1,300,000 \text{ g mL}^{-1}$ )
- An ethanol suspension (40 wt. %) of silica particles

After 1 h of stirring, the final PVP and silica particles concentrations were 10 and 20 wt. %, respectively.

The PVP/silica particles ethanol suspension was electrospun under a voltage of 30 kV at room temperature ( $23 \pm 2$  °C) and relative humidity ( $45 \pm 10$  %). A flow rate of 0.100 mL min<sup>-1</sup> was assured by the syringe pump; the solutions were electrospun over a fixed collection distance of 39 cm. To convey the electrospinning jet onto the collector, a copper string was placed at the bottom of the chamber at the same potential of the needle

nozzle. The as-prepared electrospun non-woven mats were dried out at 80 °C for 60 min and stored in a desiccator. The mats were produced in thin sheets corresponding to the content of a syringe.

A second series of samples were submitted to a proper thermal treatment. The electrospun mats were slowly heat treated, in air, from 150 to 200 °C with steps of 10 min each 10 °C. Finally, they were dried out for 6 h at 200 °C to promote thermal crosslinking of PVP and make the electrospun composite mat water-insoluble [Newsome 2014].

In the following the two series of samples that were prepared by electrospinning and heat treated, will be distinguished with the acronyms PVPSi\_NT and PVPSi\_HT and are shown in Figure 15.



Figure 15: Electrospun mats: a) PVPSi\_NT and b) PVPSi\_HT.

## 4.2.5. Electrospinning of ternary composite mats: PVP-SiO<sub>2</sub>-TiO<sub>2</sub>acac

The electrospinning solution was prepared by mixing two other ones:

- An ethanol solution of PVP (20 wt.%) and a certain amount of TiO<sub>2</sub>acac micropowder;
- An ethanol suspension of silica sol-gel particles (40 wt.%);

After 10 h of stirring, the final PVP, SiO<sub>2</sub>, and TiO<sub>2</sub>acac concentrations were 10, 20, and 5 or 20 wt.% respectively to prepare electrospun mats namely PVPSi\_5Ti\_NT and PVPSi\_20Ti\_NT.

The resulting PVP/SiO<sub>2</sub>/TiO<sub>2</sub>acac ethanol suspension was electrospun under a voltage of 40 kV at room temperature and a humidity of  $45 \pm 10\%$ . A flow rate of 0.010 mL min-1 was assured by the syringe pump and electrospinning was carried out over a fixed collection distance of 39 cm. To convey the electrospinning jet onto the collector, a copper string was placed at the bottom of the chamber at the same potential of the needle nozzle. The prepared electrospun mats were dried out at 80 °C for 1 h and stored in a desiccator. Finally, the thermal treatment of electrospun mats were carried out in air from 120 to 200 °C with steps of 10 min each 10 °C, then samples were kept for 6 h at 200 °C to promote thermal crosslinking of PVP and make the electerospun composite mat water-insoluble. The overall procedure for the manufacturing of the ternary composites is illustrated in Scheme 1.3



Scheme 1.3. Schematic representation showing the preparation of SiO<sub>2</sub>NPs and TiO<sub>2</sub>acac micro-powders, followed by preparation of ternary composite suspension and their electrospinning. Later the electrospun mats were heat treated for stabilization.

The two series of heat-treated electrospun samples will be distinguished with the acronyms PVPSi\_5Ti\_HT and PVPSi\_20Ti\_HT and ternary composite mats before and after thermal treatment are shown in Figure 16.



Figure 16: Electrospun Mats: (a) PVPSi\_5Ti\_NT, (b) PVPSi\_5Ti\_HT, (c) PVPSi\_20Ti\_NT, (d) PVPSi\_20Ti\_HT.

The compositions of suspensions and relative final products of all the studied samples are reported in Table 2.0

Sample	Suspension (wt.%)			Product (wt.%)		
Sample	PVP	SiO <sub>2</sub>	TiO <sub>2</sub> acac	PVP	SiO <sub>2</sub>	TiO <sub>2</sub> acac
PVP_tq	10	-	-	100	-	-
PVPSi	10	20	-	33	67	-
PVPSi_5Ti	10	20	5	28	57	15
PVPSi_20Ti	10	20	20	20	40	40

 Table 2.0.
 Composition (wt.%) of suspensions and relative final electrospun products.

## 4.3 Characterization of samples

The silica sol-gel particles, the hybrid  $TiO_2$  dried gels particles and all the electrospun samples were characterized by a series of analytical techniques to investigate their structural, physicochemical and functional properties. Here the instruments used, the measurement conditions and information about the elaboration of collected data are reported.

## 4.3.1. Dynamic Light Scattering (DLS)

The size distribution of silica sol-gel particles was characterized by Dynamic Light Scattering (DLS) technique at Department of Chemical Sciences of the University of Naples Federico II by Prof. Luigi Paduano.

DLS measurements were performed with a home-made instrument composed by a Photocor compact goniometer, a SMD 6000 Laser Quantum 50 mW light source operating at 532.5 nm, a photomultiplier (PMT-120-OP/B) and a correlator (Flex02-01D) from Correlator.com. All measurements were performed at  $(25.00 \pm 0.05)$  °C with the temperature controlled by means of a thermostat bath. The diffusion coefficient (D) was performed using a variation of CONTIN algorithm incorporated in Precision Deconvolve software. For spheres diffusing in a continuum medium at infinite dilution, in the approximation of spherical objects, the diffusion coefficient is related to the hydrodynamic radius (Rh), through the Stokes–Einstein equation [Kätzel 2008].

## 4.3.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

FT-IR spectroscopy was used to perform a detailed analysis of the materials structure of electrospun sample and to point out the modifications after heat treatments.

The ATR-FTIR spectra measurements were carried out at the Department of Chemical, Materials and Production Engineering (University of Naples Federico II), on a Nikolet 5700 FTIR spectrometer (Thermo Fisher, Waltham, MA, USA) using a single reflection Attenuated Total Reflectance (ATR) accessory with a resolution of 4 cm<sup>-1</sup> and 32 scans. Thermo Scientific<sup>™</sup> OMNIC<sup>™</sup> Software Suite (v7.2, Thermo Fisher, Waltham, MA, USA, 2005) was used to analyze the spectra.

# 4.3.3. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)

The morphology of the electrospun PVP\_SiO<sub>2</sub> samples was analyzed by using a field emission scanning electron microscope (FESEM, Zeiss SIGMA) with a nominal resolution of 1.3 nm at 20 kV at the Department of Physics (University of Salerno) by Prof. Antonio Vecchione. SEM images were acquired by collecting secondary electrons (SE) with an Everhart-Thornley (ET-SE) type detector, and by using SmartSEM software (v05.04.00, Carl Zeiss Microscopy GmbH, Jena, Germany, 2016). In some cases, an In-Lens (IL) detector, located inside the electron column of the microscope and arranged rotationally symmetric around the optical axis, was used to collect SEM images with higher contrast.

The morphology of the electrospun PVP\_SiO<sub>2</sub>\_TiO<sub>2</sub>acac samples was carried out by using the following tools:

- **SEM** EDX FEI – Ispect S, Column E-SEM W, Source: 200 V–30 kV, filament: tungsten equipped with an Everhart–Thornley detector (ETD); (Department of Chemical, Materials and Production Engineering - University of Naples Federico II).

- **TEM** FEI TECNAI G2 200 kV apparatus, operating at 120 kV. The samples were transferred on carbon-coated copper grids (200 mesh) by dispersing them in ethanol and then adding one drop on the copper grid and evaporating the solvent; (Department of Chemical Sciences - University of Naples Federico II).

# 4.3.4. Thermal Analysis - Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC)

- Thermal analysis of binary electrospun mats (PVPSi\_NT and PVPSi\_HT) was carried out at Department of Chemical Engineering and Chemistry of Eindhoven University of Technology).

Thermogravimetric (TGA) analysis was performed at using a TA thermogravimetric analyzer (TGA) Q500 V20,13 Build 39. The measurements were conducted in nitrogen, at a heating rate  $10 \,^{\circ}$ C min<sup>-1</sup>.

For the thermal conductivity ( $\lambda$ ) determination, a Differential Scanning Calorimetry system (DSC Q2000 V24,10 Build 122) equipped with a refrigerated cooling system was employed; TA Universal analysis software (v4.5a, TA Instruments, New Castle, DE, USA, 2018) was used for the data analysis. Tzero Aluminum Hermetic pans were used for these measurements to suppress unwanted signals (e.g., volatile eventually present) and to improve the quality of the analysis. An empty pan of the same type was used as reference in each run. Calibration of the instrument was performed with Indium.

The measurements were carried in a temperature range from -50 °C to 300 °C and the heating rate was 10 °C min<sup>-1</sup>. Four samples of PVPSi\_HT and an equal number of pure PVP were loaded in the pans. Each pan had a cross sectional diameter of 5.0 mm (cross sectional area A = 0.19625 cm<sup>2</sup>) and a height (L) of 4.0 mm; all the samples were cut into small disks with the same A and different L changing in the range 1–4 mm. The

samples preparation was performed according to methodology reported [Mettler-Toledo].

 Thermal analysis of ternary mats (PVPSi\_5Ti and PVPSi\_20Ti) was carried out at Laboratory for Advanced Fibers, Empa Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland.

Differential scanning calorimetry (DSC) of analysis of as-spun and heat-treated samples were performed on the DSC 214 Polyma instrument (NETZSCH-Gerätebau GmbH, Selb, Germany) at a ramp of 10 °C/min (20 to 300 °C) under N2 flow (50 mL/min). The glass transition temperature (Tg) of different samples was determined by using the "tangent method" [Bifulco 2020.].

Thermogravimetric analysis (TGA) was performed on a NETZSCHTG 209 F1 instrument (NETZSCH-Gerätebau GmbH, Selb, Germany) under air with a flow of 50 mL min<sup>-1</sup>. Temperature ranges from 25 to 800 °C at a ramp of 10 °C/min was used for the analysis.

## 4.3.5. Vertical bunsen burner Test for cabin and cargo compartment materials

This test method is intended for use in determining the resistance of materials to flame when tested according to the 60-second and 12-second Vertical Bunsen Burner Tests specified in Federal Aviation Regulation (FAR) 25.853 and FAR 25.855.

Three answers are evaluated:

- <u>Extinguishing time</u>: the time the specimen continues to flame after the burner flame is removed. It is required to be less than 15 s;
- <u>Drip extinguishing time</u>: the time, in seconds, that any flaming material continues to flame after falling from the specimen to the floor of the chamber. It is required to be less than 5 s (for the 12 s test);
- <u>Burn length</u>: the distance from the original specimen edge to the farthest evidence of damage to the test specimen. It is required to be less than 203 mm (for the 12 s test);

Tests are performed in a draft free cabinet fabricated in accordance with Federal Aviation Administration (FAA). It is suggested that the cabinet be located inside an exhaust hood to facilitate clearing the cabinet of smoke after each test. Stainless steel or

other corrosion-resistant metal 0.04 inch (1 mm) thick will be used for the bottom surface of the chamber.



Figure 17: Front and top view of Vertical Bunsen Burner Test Cabinet and laboratory set-up at GEVEN S.p.A.

Moreover, samples need to be installed within a metal holder so that the two long sides and the upper ones are fixed in vertical position during the test, while the flame laps the lower side. Before the test is performed, samples are placed in a conditioning room for 24 hours at a temperature of  $24^{\circ}C \pm 3^{\circ}C$  and relative humidity of  $50\% \pm 5\%$ .

The vertical bunsen burner tests were performed at Flammability Laboratory of GEVEN S.p.A.

## 4.3.6. Smoke density test

This test method is used to determine the smoke generating characteristics of airplane passenger cabin interior materials to demonstrate compliance with the requirements of FAR 25.853.

Specific optical density (Ds)-specific optical density is a dimensionless measure of the amount of smoke produced per unit area by a material when it is burned. In this test, the maximum value of Ds (200 is the maximum allowed value) that occurs during the first 4 minutes of a test,  ${}^{4}D_{m}$ , is reported.

The test chamber will be a square-cornered box with inside dimensions of  $914 \pm 3$  mm wide,  $610 \pm 3$  mm deep, and  $914 \pm 3$  mm high. A typical test chamber is shown in Figure 18. The interior surfaces will be porcelain-nameled metal that is resistant to chemical attack and corrosion and suitable for periodic cleaning. The chamber will be equipped with a door to provide convenient access for changing test samples and for cleaning the chamber walls as required. The door will have a viewing window to observe the sample and pilot flamelets behavior during a test, especially when any of the them extinguish.



Figure 18: Typical Smoke Density chamber and laboratory set-up at GEVEN S.p.A.

An electric furnace and associated controlling devices are capable of providing a constant thermal flux density of 2.5 W cm<sup>-2</sup> on the sample surface. The pilot burner will be a multiple flamelet type with six tubes having an outer diameter of 3.2 mm and an inner diameter of 1.4 mm. The two outer tubes of the pilot burner will be directed perpendicular to the surface of the sample. The two inner tubes will be directed at an angle of 45 degrees downward. The two intermediate tubes will be directed vertically downward into the drip pan of the sample holder.

The pilot burner will be centered in front of and parallel to the sample holder and the gas fuel for the pilot burner will be prepared by mixing filtered oil-free air with 95% minimum purity propane.

The sample holder will consist of a stainless-steel frame, a backing made of insulation board, a spring and retaining rod to secure the sample in place, and aluminum foil for wrapping the sample. A drip pan to catch and retain dripping material will be attached to the bottom front of the holder. A photometric system capable of detecting light transmittance values of 1% minimum to an accuracy of 0.03% will be provided. The

system will consist of a light source and photomultiplier tube that are oriented vertically to reduce measurement variations due to stratification of the smoke in the chamber during the test. The light source will be an incandescent lamp mounted in a box below the chamber floor, operated at a light brightness temperature of  $2200 \pm 100$ K controlled by a constant-voltage transformer. The box will contain the necessary optics to produce a collimated light beam  $38 \pm 3$  mm in diameter, passing vertically up through the chamber.



Figure 19: Electrospun sample set in the holder, before and during the smoke density test at GEVEN S.p.A.

A minimum of three samples will be prepared and tested for each part/construction. Samples will be conditioned at temperature of  $21^{\circ}\pm3^{\circ}$ C and  $50\%\pm5\%$  relative humidity for a minimum of 24 hours unless otherwise specified. Only one sample at a time will be removed from the conditioning chamber. When removed, the sample will be immediately tested.

The smoke density tests were performed at Flammability Laboratory of GEVEN S.p.A.

## 4.3.7. Water Resistance Test

The water resistance was evaluated accordingly to the method proposed in the literature [Rhim 2004].

Three pieces of electrospun samples were placed in a 30 mL of distilled water. After 24 h, the samples were removed and gently rinsed with distilled water. The weight of water-soluble matter, WS, was determined as:

$$WS = (S^{\circ} - S)/S^{\circ}$$
(1.13)

where  $S^{\circ}$  and S are the weights of the samples before and after immersion in water, both evaluated after drying at 105 °C for 24 h.

#### 4.3.8. Flow Resistivity

Airflow resistivity is a physical parameter, characteristic of porous and fibrous materials, which quantifies, per unit length, the ability to oppose resistance to the motion of air particles inside the material.

The experimental determination of the air flow resistivity was measured according to EN 29053-ISO 9053 [Iannace 2014] through the experimental device SCS 9023 and FOAM-X software (v.2007, Mecanum Inc., Sherbrooke, QC, Canada, 2017) used for data analysis, with the alternate airflow method formerly proposed by Whole and Weber based on a sinusoidal airflow at the frequency of 2 Hz.

The air flow characterization was performed at Department of Architecture and Industrial Design of the University of Campania Luigi Vanvitelli by Prof. Gino Iannace. The measurement device consists of a cylindrical chamber closed with the material sample, a piston system pumping air inside the chamber, while a pressure microphone measured the pressure level inside. As suggested in the ISO standard, ten measurements are performed for four different air velocities in order to determine the airflow resistance. To obtain the airflow resistivity measured in Pa it is necessary to multiply the airflow resistance by the sample thickness. It is important to state that the uncertainty associated with the flow resistivity measurement is generally large due to density change, presence of non-laminar air flow, low pressure differences on the two sides of the sample, and inaccuracy in thickness determination [Berardi 2015].



**Figure 20**: Schematic representation of the air flow resistivity measurement apparatus and laboratory setup at Department of Architecture and Industrial Design of the University of Campania Luigi Vanvitelli.

The measurement of airflow resistance, of porous and fibrous acoustical materials, is standardized in ISO 90532 and in ASTM C-5223. These Standards describe the measurement equipment and the test procedure. The airflow resistance of a material is defined as:

$$\mathbf{R} = \Delta \mathbf{p} / \mathbf{q}_{\mathbf{v}} \tag{1.14}$$

where:

 $\Delta p$  is the air pressure difference across the sample with respect to the atmosphere, in Pa,  $q_v$  is the air flow rate through the sample, in m<sup>3</sup> s<sup>-1</sup>.

Two derived quantities of great interest in applied acoustic are the specific airflow resistance, RS, and the airflow resistivity, r, defined as:

$$\mathbf{R}_{s} = (\Delta p / q_{v}) \cdot \mathbf{A} \tag{1.15}$$

$$\mathbf{r} = (\Delta \mathbf{p} / \mathbf{q}_{\mathbf{v}}) \cdot (\mathbf{A} / \mathbf{d}) \tag{1.16}$$

where:

A is the section of the tested sample, in  $m^2$ ; d is the thickness of the tested sample (considered as homogeneous) in the flow direction, in m.

The reported results are the average of three values obtained on three different samples in the shape of discs of 10 cm diameter and 1 cm thickness.

## 4.3.9. Sound Absorption coefficient measurement

The sound absorption coefficient at normal incidence, defined as the ratio between the energy absorbed to the material and the incident energy of the sound wave, indicates the ability of the porous material to absorb sound energy in different frequency bands. It

has been measured by means of an acoustic impedance tube (Kundt tube) in the frequency range 200–1600 Hz according to the geometry of the used instrument (tube diameter and microphones spacing).

The measurement setup consists of an impedance tube (a straight and rigid cylindrical pipe) composed by two main tubes: transmitting and receiving one, a loudspeaker with an amplifier, two microphones and Pulse LabShop software (v6.1.5.65, Brüel&Kjær, Nærum, Denmark, 2002). An image and a sketch of the experimental setup is reported in Figure 21. The acoustic characterization was carried out at Department of Aerospace Engineering of the University of Naples Federico II by research team of Prof. Francesco Marulo.



Figure 21: (a) Laboratory setup of acoustic sound absorption coefficient measurement; (b) Schematic of two-microphone impedance tube method.

The measurements have been performed by employing the two-microphone method (using two microphones in fixed locations) according to ASTM E 1050-12 and ISO 10534-2. The test sample (with a diameter pair to 100 mm) is mounted at one end of the impedance tube. Plane waves are generated in the transmitted tube by a loudspeaker and the sound pressures are measured at two locations near to the sample.

The complex sound reflection coefficient R of a tested sample is calculated from the corrected acoustic transfer function  $H_{12}$ . According to Chung and Blaser's [Chung 1980] results, the complex sound reflection coefficient is:

$$\mathbf{R} = \mathbf{R}_{r} + j\mathbf{R}_{i} = ((\mathbf{H}_{12} - \mathbf{e}^{(-jks)})/(\mathbf{e}^{jks} - \mathbf{H}_{12}))\mathbf{e}^{(2jk(s+L))}$$
(1.17)

where Rr and Ri are respectively real and imaginary part of complex acoustic reflection coefficient (R), k is wave number, and it is equal to  $2\pi f/c$  (f is the working frequency, c is the sound speed in the air), L distance from the test sample to the center of the nearest microphone, s center-to-center spacing between microphones, and  $j = \sqrt{(-1)}$ . From equation (1.17), it is possible to calculate the sound absorption coefficient at normal 67 incidence as a function of frequency [Chung1980, Koruk 2014] and the normal acoustic specific impedance respectively as:

$$\alpha = 1 - |\mathbf{R}|^2 = 1 - \mathbf{R}_r^2 - \mathbf{R}_i^2$$
(1.18)

$$Z/Z_0 = r/(\rho 0 c 0) + jx/(\rho 0 c 0) = ((1 + R)/(1 - R))$$
(1.19)

where  $Z0 = r/(\rho 0 c0)$  is the characteristic impedance of the medium with p0 and c0 respectively density and speed of sound in the air,  $r/(\rho 0 c0)$  is the normal specific acoustic resistance ratio and  $jx/(\rho 0 c0)$  is the normal specific acoustic reactance ratio. The normal incidence surface impedance, indeed, is a complex coefficient given by the acoustical pressure to velocity ratio at the surface of the tested sample when it is excited by a normal incidence acoustical wave. It measures the resistance and inertia encountered by the acoustical wave trying to penetrate the material. Its real part is the acoustical resistance and its imaginary part is the acoustical reactance.

The analysis was made in the following manner. It was performed, at first, on one disk. Then the other disks were added, one by one. After each addition, a pressure was exerted through a metal disk of 130 g for one minute in order to be sure that the disks adhered to each other and to completely eliminate the air layer that could remain entrapped between the electrospun disks. After the measurements, the disks could be easily separated and reassembled in a different order, thus proving that no connection was established between them. The pile of disks was simply leant against the bottom of the acoustic impedance tube. Each measurement was repeated 3–5 times (the test sample was removed and reinserted in the impedance tube each time) and the final result was an average of the repeated measurements. Figure 22 shows the photograph of the final pile of disks prepared for the acoustic impedance tube.



Figure 22. PVPSi\_NT electrospun piled mats inside the impedance tube before acoustic measurements.

# 4.3.10. Artificial neural network-based models for predicting the sound absorption coefficient

Machine Learning groups techniques and mathematical models for the formulation of complex algorithms, impossible to model through a traditional approach. Machine learning based algorithms have been used to solve problems of different nature [Iannace 2019]. Artificial neural networks, a set of algorithms for classification and regression, have been widely used. Neural networks try to imitate the structure and functioning of the biological brain, made up of large groups of neurons connected by axons. Individual neural units, called artificial neurons, are interconnected with each other to form a network. Crucial point of this technology is the connection between individual neural units which can be reinforcing or inhibiting. This action is exercised through a combination of the input values and an activation function, which returns the output of the neuron [Ripley 2007].

Neural networks are nonlinear mathematical functions that transform a set of independent variables  $x = (x_1,...,x_n)$ , defined as network inputs, into a set of dependent variables  $y = (y_1,...,y_k)$ , which represents he network output. The result obtained depends on a set of values  $w = (w_1,...,w_n)$ , called weights. The relationship between output and input of the network can be represented through the following equation:

$$y = f\left(\sum_{j} w_{j} * x_{j} + b\right) \tag{1.20}$$

Here:

- $x_i$  is the j<sup>th</sup> input
- w<sub>j</sub> is the j<sup>th</sup> weight
- b is the bias
- y is the output

The weights and biases contain the information that the neuron recovers during the training phase and that it will use later to act incongruent situations. The function f represents the activation function: It is generally a threshold function that activates only neurons with signals compatible with the threshold, in this way the signal is transferred to the next neuron or neurons. Nonlinear stepped, sigmoid or logistic functions are examples of activation functions [Ripley 2002]. As anticipated, the weights are adjusted during the training phase through an iterative procedure. This procedure requires intense
computational effort and uses a certain number of input-target pairs, called training sets. In training, we search for the values of weights that minimize a specific error function [Møller 1993]. The architecture of a neural network is made up of three parts, containing distinct quantities of neurons:

- An input level
- Several hidden levels
- An output level

The input signals pass from the input level to the output level through the neurons of the internal layers, as shown in the following Figure 23.



Figure 23. Artificial Neural Network architecture with layer, nodes and connections.

The network introduces external signals through the layer of input nodes, each of which is connected to each node of the hidden layer. Each node processes the received signals by applying the transfer function and transmits the result to the subsequent nodes.

The success of a prediction model based on machine learning essentially depends on the quality of the input data. The input data can contain anomalies that during the training phase can detect false trends that reduce the prediction ability of the model. To avoid this, it is necessary to identify these anomalies in the preprocessing phase and work them properly. The dataset contains the results of the sound absorption coefficient measurements, and before proceeding it is necessary to check the presence of possible missing attributes or records, the presence of records without values or the presence of values available only in aggregate form. Since the input data contains different variables (weight, frequency, sound absorption coefficient), the resizing of the data is necessary.

When the input variables are characterized by different units of measurement, they have very different ranges of values that can attribute a different weight. Standardizing the variables is of fundamental importance for the success of the model. This procedure makes the variables comparable even if they belong to different distributions, or if expressed in different units of measurement. Standardization consists of a double normalization: first, each datum is transformed in its deviation from the average, then the identified gap is transformed into the number of standard deviation units. In this way, the uniqueness of the points and the relative distances from any other point are preserved. As mentioned, standardization transforms the original data into deviations from the average, being the algebraic sum of the deviations from the average equal to zero, then all the standardized variables have an average of zero value. Furthermore, this procedure divides each gap from the mean by the standard deviation, so the standard deviation of a standardized variable is equal to 1. In this work the standardization of the z score was adopted. In this way, the average of the column was subtracted from each value contained in it and the result was divided by the standard deviation of the column. Standardization was performed through the following formula:

$$\mathbf{x}_{\text{scaled}} = (\mathbf{x} - \text{mean}(\mathbf{x})) / \text{sd}(\mathbf{x}) \tag{1.21}$$

Here:

- mean(x) is the mean of the x
- sd(x) is the standard deviation of the x

In summary, with standardization the above average values become positive scores, while the below average values become negative scores. Moreover, the score obtained is deprived of the dimensions, by subtracting the mean of the distribution and dividing the result by the standard deviation of the same [Iannace 2020].

# 4.3.11. Zeta Potential

The streaming surface potential of heat-treated electrospun samples was measured by a SurPASS 3 electrokinetic analyzer (Anton Paar) equipped with two  $10\times20$  mm sample holders. Electrospun mats mounted on two rectangular sample holders are placed parallel to each other at a distance of ~100 µm to form a channel. Then, the streaming potential was measured the change in potential between two electrodes at end of the channel as a function of the electrolyte pressure.  $10^{-3}$  M KCl was used as the electrolyte and the pH of the electrolyte was automatically controlled using a stock solution of 0.1

M HCl and 0.1 M NaOH with the help of the titrator and data were recorded using SurPASS 3 software.

#### 4.3.12. Electron Paramagnetic Resonance (EPR) spectroscopy

EPR spectroscopy allowed to detect and identify paramagnetic species, such as the superoxide radical anion, on the studied materials. The analyses were performed at the Department of Chemical Sciences of the University of Naples Federico II by Prof. Gerardino D'Errico, using an X-band (9 GHz) Bruker Elexys E-500 spectrometer (Bruker, Rheinstetten, Germany). The capillary containing the powered sample was placed in a standard 4 mm quartz sample tube. The temperature of the sample was regulated at 25 °C. The instrumental settings were as follows: sweep width, 140 G; resolution, 1024 points; modulation frequency, 100 kHz; modulation amplitude, 1.0 G; time constant, 20.5 ms. EPR spectra were measured with attenuation of 10 dB to avoid microwave saturation of resonance absorption curve. Usually, 16 or 32 scans were accumulated to improve the signal-to-noise ratio. In the case of samples giving a very intense signal, the detector gain was lowered from 60 to 40 dB. The g values and the spin density of the samples were evaluated by means of an internal standard, Mn<sup>2+</sup>- doped MgO. The values were calibrated in reference to TEMPOL (4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxyl) and DPPH (2,2-diphenyl-1-picrylhydrazyl) solutions.

A suspension of electrospun sample (previously powdered) was prepared (10 g/L) in water and kept stirring in the dark. Then DMPO aqueous solution was added, so to obtain a DMPO concentration of 25 mM. After 1 min, the samples were centrifuged and the spectra of the supernatants were registered with an attenuation of 15 dB. Several scans were accumulated to improve the signal-to-noise ratio. The spectra were corrected, when needed, subtracting the contribution of the DMPO dimeric adduct.

#### 4.3.13. Dye removal Test

The electrospun composite samples were investigated for the removal of a model pollutant like Methylene Blue (MB) from an aqueous solution.

A piece of the mat was inserted into a glass vial containing MB solution (initial concentration  $C_0 = 10 \text{ mg/L}$ ) at 1 g/L electrospun mat loading at neutral pH and the experiment was carried out in the dark at room temperature for 6 h. Periodically, the intensity of MB absorption peak (at  $\lambda = 664 \text{ nm}$ ) was recorded by a Shimadzu UV-2600i spectrometer and the concentration of MB in the solution was calculated using a

calibration curve. The MB removal % was calculated using equation (1.22), where C is the MB concentration at a given time:

MB removal 
$$\% = 100 \cdot (C_0 - C)/C_0$$
 (1.22)

# 5.0 Results and Discussion

# 5.1 Electrospun binary composites as sound absorber for aerospace applications: PVP\_SiO<sub>2</sub>Np

# 5.1.1. Silica sol-gel particles

As mentioned above, the Stöber method is a sol-gel synthesis in alkaline environment and is able to give monodisperse sub-micrometric silica gel particles, also a few nanometers in diameter, through the well-known hydrolysis and poly-condensation reactions (Section 1.1.)

The sol-gel SiO<sub>2</sub>Np ethanol suspension was characterized by means of DLS (Dynamic Light Scattering) to investigate the SiO<sub>2</sub> particles aggregation state. As reported in Figure 24 the SiO<sub>2</sub>Np ethanol suspension is indeed composed by a single population of particles with a mean hydrodynamic radius (Rh) of about  $140 \pm 60$  nm.

The Light Scattering technique confirmed the satisfactory obtaining of monodisperse silica particles through Stöber method.



Figure 24. Hydrodynamic radius distribution obtained from DLS measurements for the sol-gel SiO<sub>2</sub>Np suspension in ethanol.

# 5.1.2. Morphological structure and composition

# **SEM** analysis

As described above, two kinds of samples were considered: electrospun mats that was not heat treated (PVPSi\_NT) and heat-treated ones (PVPSi\_HT).

Figures 25 and 26 show the SEM micrographs of both representative samples.



**Figure 25.** SEM micrographs of bare electrospun mat (PVPSi\_NT) at different magnifications: a) 10 μm, b) 2 μm.



**Figure 26.** SEM micrograph of heat treated mat (PVPSi\_HT) at different magnifications: a) 10 μm, b) 200 nm.

Figure 25 refers to sample PVPSi\_NT at different magnifications. Analogously Figure 26 refers to sample PVPSi\_HT at different magnifications. The samples show the characteristic fibrous structure of electrospun materials, without the formation of beads-on-string [Koombhongse 2001]. As can be seen, the fiber structure is different than the one reported by Newsome et. al [Newsome 2014]. This consequence can be attributed

to the different process parameters [Newsome 2014] used during PVPSi\_NT mats production.

Figure 25 b shows, in fact, a bimodal distribution of the fiber diameter:  $1.6 \pm 0.4 \mu m$ , close to the one reported for PVP pure mats [Avossa 2008], and  $330 \pm 30 nm$ , close to the one reported by Newsome et al. [Newsome 2014]. Figure 26 shows that after thermal treatment a part of the fibers was broken. This allows us to have a glance in the interior of the fibers (see Figure 26 b): the particles appear to be tightly arranged inside the fibers and separated by thin polymer layers. This may be the consequence of strong absorption interactions between the organic and the inorganic phases. It is reported [Bogatyrev 2001, Toki 1992] that strong hydrogen bonds are expected to form between silanols groups (-Si-OH) present on the surface of silica particles and carbonyl groups of PVP (whose repetitive unit is reminded in Figure 12).

#### **Density and Porosity of Electrospun Mats**

In Table 3.0 the fiber diameters are reported altogether with the densities, porosity and flow resistivity of PVP, PVPSi\_NT and PVPSi\_HT blankets. The values for bare PVP were taken from a previous work [Avossa 2018].

The values of density,  $\rho_s$ , were estimated with picnometer using hexane. The apparent densities,  $\rho$ , were estimated by the volume and weight of a pile of disks like the one showed in Figure 22. The porosity, that is the ratio of pore volume,  $V_p$ , to bulk volume, V, was calculated with the formula:

$$P = V_p / V = 1 - \rho / \rho_s$$
 (1.23)

The fiber density,  $\rho_{s}$ , doubles on addition of silica. This is clearly due to the greater density of silica with respect to bare PVP. Although this may lead to a greater apparent density (see value for PVPSi\_NT), a greater porosity and therefore a more open mat structure is obtained when silica is added.

#### **Flow Resistivity**

The addition of silica makes the flow resistivity value of sample PVPSi\_NT to increase with respect to the pure PVP mat. This may be the consequence of the presence of the second family of fibers with a diameter  $330 \pm 30$  nm with a much higher specific surface (see Figure 25) which is absent in the pure PVP mat [Avossa 2018]. The decrease in the

heat-treated sample (PVPSi\_HT) may be probably ascribed to the increase of mat looseness linked to the observed fiber breakage (see Figure 26) which occurs during the thermal treatment.

It is worth observing that the experimental values of electrospun PVP and PVPcomposites are much greater than the ones  $(1-40 \text{ kPa} \cdot \text{s/m}^2)$  reported for glass wool [Tarnow2002, Stani 2005] which is widely applied for thermal and noise control in the side wall of aircraft cabins.

The flow resistivity results show that the electrospun composite, formed by the addition of silica nanoparticles to the PVP solution, has better air flow resistance compared to bare electrospun PVP and glass wool (e.g. Microlite®).

**Table 3.0.** Fiber diameter, densities, porosity and flow resistivity values of PVP, PVPSi\_NT and PVPSi\_HT blankets.

	Fiber Diameter [µm]	Apparent Density ρ [g/cm³]	Density ρ <sub>s</sub> [g/cm <sup>3</sup> ]	Porosity [%]	Flow Resistivity [kPa (s/m²)]
PVP	$1.6\pm0.4$	0.063	1.06	94	440
PVPSi_NT	$\begin{array}{c} 1.6\pm0.4\\ 0.33\pm0.03\end{array}$	0.071	2.08	97	783
PVPSi_HT	$\begin{array}{c} 1.6 \pm 0.4 \\ 0.33 \pm 0.03 \end{array}$	0.042	2.12	98	289

### **ATR-FTIR** spectroscopy analysis

Figure 27 shows the FTIR spectra of PVPSi\_NT (red line), PVPSi\_HT (green line) and bare PVP (blue line).



Figure 27. FTIR spectra of PVP\_SiO<sub>2</sub>NT (red line), PVP\_SiO<sub>2</sub>HT (green line) and pure PVP (blue line).

In the spectrum of Figure 26 (blue line) the characteristic PVP bands are observed:

- 2930 and 2850  $\text{cm}^{-1}$  CH stretching
- 3460 cm<sup>-1</sup> OH stretching
- $1650 \text{ cm}^{-1} \text{ C} = \text{O}$  symmetric stretching
- $1422 \text{ cm}^{-1} \text{ CH}_2$  in-plane bending
- 1286 cm<sup>-1</sup> CN stretching

They are all present in the spectra of Figure 27 altogether with the ones characteristic band of silica (1050  $\text{cm}^{-1}$  Si-O-Si stretching) showed for composite sample (green and red line).

When comparing Figure 26 (red line) and (green line) a general reduction of intensity of the PVP bands with respect to silica is observed after thermal treatment. In addition to the typical stretching band of carbonyl group at 1650 cm<sup>-1</sup>, a new band at 1700 cm<sup>-1</sup> also appears after the thermal treatment (as shown in the magnification of the Figure 27). This band may be attributed to stretching vibration of carbonyl groups in a different environment than the one indicated by the band at 1650 cm<sup>-1</sup> [Bogatyrev 2001]. It is known [Loría-Bastarrachea 2011, Peniche 1993] that thermal degradation of PVP in nitrogen atmosphere occurs at high temperatures, 400–500 °C, with depolymerization of PVP monomer of the polymeric chain. It was also reported, however [Bogatyrev 2001, Peniche 1993], that in oxidative environment, thermal degradation at temperatures over 200 °C, does occur involving partial removal of side pyrrolidone rings and double

bond formation along the polymer chain. The band at 1700 cm<sup>-1</sup> may be attributed just to stretching of the carbonyl groups conjugated to the double bonds [Bogatyrev 2001] of the polyenic chains that, consequently, form.

Furthermore, the reduction of flexibility due to these cross-links and a brownish color were reported to appear [Bogatyrev 2001].

It is worth pointing out that, after thermal treatment, PVPSi\_HT electrospun samples consistently acquired a brownish color (see Figure 15b), moreover a slight mass change (2.54 wt. %) was recorded.

### Water Resistance

The water-solubility would make completely useless this soundproofing material in the aeronautic field, in fact, PVP is soluble in water and many alcohols, which limits the applicability of electrospun PVP-based nanofibers. The PVPSi\_NT composite was crosslinked in a heater at low relative temperatures (120°C) to investigate the effect of thermal crosslinking on solvent stability. During thermal treatment has been no observed swelling or difference of sample morphology.

A non-water solubility test was performed in order to confirm the water resistance of thermal crosslinked sample PVPSi\_HT compared to the non-treated one PVPSi\_NT. The experiment has been performed by immersing the PVPSi\_NT and PVPSi\_HT samples in distilled water. The Figure 28 illustrates three moments of the water solubility test.

In detail: frame 1 represents the initial moment (t = 0sec) of the test; frame 2 (t = 3sec) show how the sample PVPSi\_NT starts dissolving after three seconds and finally the frame 3 represent his complete dissolution after 10 second.

The Water Resistance test show that heat-treated sample PVPSi\_HT is non water soluble and its shape remains unaltered after water immersion; the good water resistance may be attributed to cross-linking occurring during thermal treatment.

The solvent-resistance and flexibility of the crosslinked nanofibers makes the electrospun composite PVPSi\_HT an ideal material to use even in environments with a high humidity rate.



**Figure 28.** Water resistance test: PVPSi\_NT on the left and PVPSi\_HT on the right. Each frame represents a moment of the test in seconds: frame 1 t=0, frame 2 t=3, frame 3 t=10.

# 5.1.3. Thermal Analysis

### Thermogravimetric analysis (TGA)

Figure 29 shows the thermogravimetric curves, recorded in nitrogen atmosphere, of PVP and PVPSi\_HT electrospun samples. The PVP shows mass changes below 200 °C that can be attributed to absorbed water release. The greater mass loss shown above 380 °C is, instead, due to its thermal decomposition that is completed at 460 °C.

The TGA curve of PVPSi\_HT samples show the same effects at 460 °C but mass changes are also observed at higher temperatures. These last mass changes may be attributed to the fact that the Stöber method provides gel silica particles. At higher

temperatures, volatiles are expected to be released as the consequence of completion of condensation reactions and sintering of the very fine silica gel particles [Brinker 1990].

It is worth underlining that the residue at 460 °C is 66% well corresponding to the expected silica content of the fibers on the basis of the composition of electrospun solution reported in Section 4.2.4.



Figure 29. TGA curves of electrospun PVP and PVPSi\_HT.

#### Thermal Conductivity by Differential Scanning Calorimetry (DSC)

Recently several papers proved that thermal conductivity can be measured through a thermal analysis apparatus such as DSC [Mettler-Toledo, Hu 2007]. Some methods use a pure metallic thin disk put on the top of the sample and of its melting to control the temperature of the sample top. Other methods obtain the same control through the addition of a thermal reservoir with temperature sensors. The first ones allow us, of course, to measure the thermal coefficient at the melting temperature of the metal but provide simple and rapid measurements. Thermal conductivity is evaluated from the slope of the endothermic peak appearing when the melting temperature of the metal is reached. Figure 30 shows the thermogram recorded in the present case. The curve shows a characteristic linear trend during melting and decreases after melting is complete, as is reported elsewhere [Mettler-Toledo]. As can be seen, the onset occurs at the

temperature of melting of the metal used in the present case (Indium: melting point 156 °C). The thermal conductance, which is the reverse of thermal resistance, R, can be calculated as the ratio of  $\Phi$  and  $\Delta$ T, taken as indicated in Figure 30. If  $\lambda$ , A and L are respectively the thermal conductivity, the section and length of the sample, the thermal resistance is proportional to the ratio L/A: R = L/ $\lambda$ A. When the measure is repeated on samples of different ratio L/A, the plot of R as a function of L/A is linear and the thermal conductivity can be measured from its slope [Mettler-Toledo].

As can be seen, a linear plot was obtained in the present case (Figure 31). The analysis gave a value of 0.044 W m<sup>-1</sup> K<sup>-1</sup> for the PVPSi\_HT sample, lower than the one for PVP, 0.084 W m<sup>-1</sup> K<sup>-1</sup> (not showed in Figure 30). This value was quite close to the one reported in the literature for pure PVP, 0.12 W m<sup>-1</sup> K<sup>-1</sup> [Wang 2012].

It is worth pointing out that the value calculated for PVPSi\_HT is close to the one (0.061 W m<sup>-1</sup> K<sup>-1</sup> at 149 °C) reported for Microlite<sup>®</sup>AA, a well-known aircraft acoustical and thermal insulation material [Manville, J. OEM Insulations Division. www.jm.com.].



Figure 30. Thermogram recorded by DSC in the case of PVPSi\_HT.



Figure 31. Plot of the thermal resistance, R, as a function of the ratio of the length, L, and section, S of the sample PVPSi\_HT.

# 5.1.4. Fire behavior of Electrospun Composite PVPSi\_HT

In order to guarantee adequate security levels in civil aviation, the international certification authorities require the execution of a certain number of tests to demonstrate that materials employed onboard satisfy specific requests when exposed to heat sources or flames. These tests (e.g. Vertical Bunser Burner and Smoke Density) reproduce critical situations that materials could afford during their operational life.

#### Vertical Bunsen Burner test results

The aircraft internal paneling must consist of materials with flame self-extinguishing propriety when they undergo a Vertical Test for 12 seconds. This test is performed in order to obtain the *burn length* measure that represents the distance between the heat source application point and the position where flame damages are detected, including partially or completely consumed, carbonized and crushed zones, and excluding spotted, faded or deformed ones outside the heat source exposition area.

The Federal Aviation Administration (FAA) regulation imposes a burn length that doesn't exceed 15 cm, furthermore, once the flame has been removed, fire must

extinguish in no more than 15 seconds on the sample and no more than 3 seconds on the drip material produced by combustion.

In order to determines the resistance of PVPSi\_HT to flame, the sample was submitted to the Vertical Bunsen Burner Test [Horner 2000].

Figure 32 show the sample PVPSi\_HT before and after the Vertical Test. According to the regulations discussed above, the test was successful because the burn length does not exceed 15 cm. So as shown in Table 4.0, the three samples submitted to the Vertical Bunsen Burner test all satisfied the requirements. In particular, no dripping was observed.

The good self-extinguishing properties may be attributed to the structure consisting of tightly assembled silica particles and to the partial thermal degradation that occurred during heating until the temperature reached 200 °C.



Figure 32. Heat-treated sample PVPSi\_HT before and after the Vertical Bunsen Burner Test.

	I T <sup>2</sup> (s)	E T <sup>3</sup> (s)	Burn Length (mm)	<b>D E T</b> <sup>4</sup> (s)	M F T <sup>5</sup> (°C)	Coupon size (cm <sup>3</sup> )	Weight (g)
Sample 1	12	0	57.1	No Drip	843	7.5 imes 0.1 imes 20	1.3
Sample 2	12	0	70.3	No Drip	843	$7.5\times0.1\times\\20$	1.2
Sample 3	12	0	50.8	No Drip	843	7.5 imes 0.1 imes 20	1.1
Results <sup>1</sup>	/	0	$59.4\pm206$	No Drip	/	/	/

**Table 4.0** Vertical Bunsen Burner Test for Cabin and Cargo Compartment Materials (Federal Aviation Regulation FAR 25.853 and FAR 25.855).

<sup>1</sup> (according to FAR 25.853, FAR 25.855), <sup>2</sup> (Ignition Time), <sup>3</sup> (Extinguishing Time), <sup>4</sup> (Drip Extinguishing Time), <sup>5</sup> (Minimum Flame Temperature).

#### **Smoke Density Test Results**

The Smoke Density test [Horner 2000] is a measure of the characteristics of the smoke that may be generated in an airplane passenger cabin. The Specific Optical Density (Ds) is a dimensionless measure of the amount of smoke produced per unit area by a material when it is burned. This is an important test because smoke excessively dense prevents us from seeing escape routes and may provoke panic.

So as shown in Table 5.0, the medium measured Specific Optical Density was 32.3 much lower than the maximum allowed value of 200, according to FAR 25.853.

	Specific Optical Density (-)	Coupon Size (cm <sup>3</sup> )	Weight (g)
Sample 1	33.2	$7.3\times0.5\times7.3$	1.1
Sample 2	32.8	$7.3\times0.5\times7.3$	1.2
Sample 3	30.9	$7.3\times0.5\times7.3$	1.3
Results <sup>1</sup>	$32.3\pm3.02$	/	/

**Table 5.0.** Smoke Test for Cabin Materials FAR 25.853.

<sup>1</sup> (According to FAR 25.853).

# 5.1.5. Acoustic Properties

# Acoustic impedance tube analysis

The acoustic impedance tube analysis allowed us to measure the normal incidence sound absorption coefficient in the frequency range 200–1600 Hz, where the performance of traditional porous materials is usually poor [Langfeldt 2019]. Figures 33 and 34 show the results of acoustic impedance analysis represented as plot of absorption coefficient,  $\alpha$ , vs. frequency (Hz).



**Figure 33.** Plots of the sound absorption coefficient vs. frequency for various PVPSi\_NT disks piles. The a, b, c, d, e and f curves refer, respectively, to samples of total mass 2.25 g, 5.13 g, 7.11 g, 11.24 g, 18.37 g and 28.25 g.



**Figure 34.** Plots of the sound absorption coefficient as a function of frequency for various PVP\_SiO<sub>2</sub>HT disks piles. The a, b, c, d, e and f curves refer, respectively, to samples of total mass 0.98 g, 2.942 g, 4.55 g, 7.28 g, 18.93 g and 26.41 g.

Figures 12 and 13 show that the addition of silica as the successive heat treatment does not change the general trend reported for the pure PVP blankets [Avossa 2018]. The absorption coefficient of one disk (curve a) is very low in the examined frequency range.

The values of  $\alpha$  increase when the disks are stacked on each other. For a total mass of about 5 g (see curve b in Figure 33 and curve c in Figure 34), it appears that the acoustical response of the samples is represented by a bell-shaped curve, in relation to a Helmholtz-type resonance, with a maximum  $\alpha > 0.9$ . The curves shift towards lower frequency and become sharper by increasing the number (and total mass) of the disks. A second relative maximum was observed for some curves. The second maximum of curves occurred at a frequency of about 3 times greater than the one of the first maximum may be imagined, even if only the growing part of it is seen. The curves for lower masses might be shifted too much towards higher frequencies to allow for observing the second maximum (beyond 1600 Hz). It is worth underlining that, keeping the total mass constant, when the analysis is repeated changing the order of the disks no differences are observed: the result is thereby related to the total mass, not to the number nor the specific identity of the piled disks.

The measurement was repeated by progressively adding one disk at a time to the pile.

The frequency for which  $\alpha$  reached the maximum value was determined for each curve. This frequency is reported in Figure 35 as a function of the mass per unit surface of the disks progressively stacked on each other. Figure 14 shows how the shift of the bell-shaped curves towards lower frequencies can be continuously tuned by changing the mass of the blanket.



Figure 35. Plots of the frequency of the sound absorption maximum versus the mass per unit surface of the piled disks.

It is worth underlining a remarkable result: very high sound absorption coefficients were measured. Comparable values of the absorption coefficient, in the 200–1000 Hz frequency range, were reported [Arenas 2010] for heavier and/or thicker samples.

This is confirmed by Figures 36 and 37 where the sound absorption curves of electrospun PVP/silica mats and glass wool samples marketed in civil and aerospace engineering fields are compared. In Figure 36, the comparison is made between samples of similar mass. In Figure 37 the results for samples of similar thickness are compared. Figure 36 shows that the electrospun PVP/silica samples may have better sound absorption properties, in the lower frequency range, than materials of the same mass that are usually traded in the field of civil engineering. However, Figure 37 shows that electrospun PVP/silica samples may have better sound absorption properties, and the field of civil engineering. However, Figure 37 shows that electrospun PVP/silica samples may have better sound absorption properties, in the lower frequency range, that are ordinarily used in the civil and aerospace engineering fields.



**Figure 36.** Comparison of the acoustical behaviors of electrospun PVP/silica mats and glass wool samples marketed in civil and aerospace engineering fields of same mass (7,.85 g).



Figure 37. Comparison of the acoustical behaviors of electrospun PVP/silica mats and glass wool samples marketed in civil and aerospace engineering fields of same thickness (2.5 cm).

Different aircraft have different noise levels and frequencies to be considered in noisereduction systems. It is also difficult to absorb or transmit the sounds at various frequencies (low, mid, and high) using existing technologies. Figure 38 shows the schematic interactions of sound waves in large porous (smaller surface area, eg. glass wool) and nanoporous surfaces (higher surface area, eg. electrospun mats). In these drawings, the sound molecules will interact more with the higher–surface area material than the–smaller surface area material (conventionally used). Thus, sound energy will turn into heat quickly with lesser nanoporous materials. The use of nanoporous high surface material, such as electrospun PVPSi ones, will reduce the amount of noise absorbers used for interior noise reduction of the aircraft.



Figure 38. Schematic views of sound interactions: (a) smaller–surface area materials; (b) higher–surface area materials

#### Simulation model results

In this study has been develop an algorithm based on neural networks to predict the values of the sound absorption coefficient. The simulation model is based on a feed-forward multi-level artificial neural network, with an input layer with two variables (mass, frequency), 1 hidden layer with 10 neurons and an output layer with a single neuron that returns the sound absorption coefficient of the material. To improve the performance of the model, the conjugated gradient backpropagation algorithm in scale [Møller 1993] was used. This algorithm returns a linear convergence in most problems, returning high performance with at least an order of magnitude faster than the generic Backpropagation algorithm. Figure 39 shows the architecture of the model based on neural networks. In the Fig. 6 the structure of each layer of the neural network is represented. The input level is composed of 2 data inputs as follows: mass of the samples, and frequency. The hidden layer contains ten neurons. The output level contains only one neuron which returns the sound absorption coefficient.



Figure 39. Artificial neural network model architecture with three layers.

Table 6.0 shows the Root Mean Squared Error (RMSE), Mean Absolute Error (MAE) and the Person's correlation coefficient for the best simulation model obtained in this study. From the analysis of Table 6.0 we can see that the simulation model based on neural network algorithm return low error and a high correlation between simulated data and measured data. To visualize the results, we will compare the bell-shaped curve of

the acoustic absorption coefficient obtained from the measured values and those simulated with the neural network model.

RMSE	MAE	Person's Correlation Coefficient
0.077	0.057	0.942

**Table 6.0** RMSE, MAE and the Person's correlation coefficient for the simulation model.

Figure 40 shows the curves returned by the simulation model fit well on those of the measured values. In correspondence with anomalies due to the uncertainties of the measurements, they manage to simulate the behavior of the material, leaving out these imperfections. In detail, in the sequence of simulated materials characterized by their increasing weight, we can see how the model manages to predict changes in the acoustic behavior of the material. In fact, the model provides the typical shape of a bell curve for the sound absorption coefficient versus frequency. Furthermore, it is confirmed that the maximum of the curve of the sound absorption coefficient increases as the mass increases, just as it is confirmed that this maximum shifts towards lower frequencies as the mass of the sample increases. For each sample shown in Figure 40, the simulation model slightly underestimates the maximum value.

Composite materials have been the subject of interest and considerable development by some industrial sectors due to the high mechanical and chemical properties, accompanied by high stiffness / weight ratios. Thanks to the small size of the sections with diameters from a few microns to fractions of a millimeter, the fibers have very high flow resistance characteristics. This result is a direct consequence of the so-called 'dimensional effect': in reduced sections the possibility of having imperfections is extremely less than when you have macro dimensional elements. Long fiber-based materials are more suitable in the production of axial-symmetric components or in any case of simple shape, while those based on short fibers can allow the modeling of more irregular-shaped parts [Trematerra 2014].



Figure 40. Measured (blue) versus simulated (red) curve of the acoustic absorption coefficient.

# 5.2 Electrospun ternary composites with adsorbed superoxide radicals for environmental applications: PVP\_SiO<sub>2</sub>Np\_TiO<sub>2</sub>acac

# 5.2.1. Structural and Thermal Analysis

# **ATR-FTIR**

The chemical structure of the electrospun fiber mats was investigated by ATR-FTIR spectroscopy. The ATR-FTIR spectra of PVP\_tq, heat-treated binary (PVPSi\_HT), and ternary (PVPSi\_5Ti\_HT and PVPSi\_20Ti\_HT) composite mats are shown in Figure 41. All samples displayed the characteristic PVP bands at 1650 cm<sup>-1</sup> (C=O symmetric stretching), 1422 cm<sup>-1</sup> (CH<sub>2</sub> in-plane bending), and 1286 cm<sup>-1</sup> (CN stretching). In addition, the spectra of samples containing silica showed the characteristic band of Si-O-Si stretching at 1080 cm<sup>-1</sup>. In the case of PVPSi\_20Ti\_HT, broadening of the bands around 550 cm<sup>-1</sup> and 660 cm<sup>-1</sup> ascribed to the Ti-O-Ti vibration was observed [Vives 2008]. Besides, the increased intensity of the band at 1545 cm<sup>-1</sup> can be assigned to enol

C=C stretching of acetylacetonate (acac) [Diaz-Acosta 2003]. Though much less pronounced, the same bands were also observed for PVPSi\_5Ti\_HT. Although most IR bands of TiO<sub>2</sub>acac were overlapped by PVP bands, the identification of C=C stretching band of acac demonstrates the stability of the Ti-acac complex after thermal treatment (at 200  $^{\circ}$ C) [Sannino 2015, Imparato 2021].

The broad band from about 3700 to 3000 cm<sup>-1</sup> is related to O-H stretching involved in hydrogen bonding of different strengths. These interactions occur between the carbonyls of pyrrolidone with the adsorbed water molecules for PVP\_tq and also with the residual -Si-OH and -Ti-OH groups in the heat-treated composite mats. For the latter samples, the shift to lower frequencies of this band is related to the strengthening of the H-bonds [Aronne 2007]. These physical interactions improve the interface between the inorganic phase and polymer matrix [Al-Harbi 2016, Zheng 2000]. This phenomenon is also promoted by abundant surface hydroxylation which is typical of sol-gel oxides.



**Figure 41.** FTIR spectra of (a) PVP\_tq (b) PVPSi\_HT, (c) PVPSi\_5Ti\_HT, and (d) PVPSi\_20Ti\_HT in the region of O-H stretching (2000-4000 cm<sup>-1</sup>) and vibrational modes of main functional groups (500-1950 cm<sup>-1</sup>).

#### 5.2.2. Thermal Analysis

### **TGA and DSC**

The thermal behavior of ternary electrospun composites has been investigated through DSC and TGA to study the effect of hybrid titania on the PVP matrix. In the previous Section 5.1.2., has demonstrated that the presence of silica increased the dimensional stability of the electrospun mats during heat treatment. In Figure 42a, DSC thermograms

of PVP\_tq, PVPSi\_NT, PVPSi\_5Ti\_NT, and PVPSi\_20Ti\_NTat different TiO<sub>2</sub>acac load are reported.



Figure 42. Thermal characterization of electrospun mats: (a) DSC curves of PVP\_tq and PVPnot treated composites, (b) TGA curves of PVP\_tq and PVP-heat treated composites, (c) DTG curves of PVP\_tq and Heat Treated Electrospun Samples

 $PVP_tq$  shows a  $T_g$  of 175 °C which is in agreement with the literature [Elishav 2018]. Figure 42a shows a slight increase of  $T_g$  for samples containing silica and hybrid titania compared to the pristine one (PVP\_tq). This effect may be due to the presence of physical interactions between hydroxyl groups and pyrrolidone (see Section 4.1), which reduce the mobility of polymer chains in composites [Al-Harbi 2016]. On the other side, figure S1 reveals that the thermal treatment does strongly affect the glass transition temperature and thus the corresponding slope change becomes not detectable. This phenomenon may be explained by taking into account two contrasting effects: the cross-link of polymer chains [Bogatyrev 2001] and the partial degradation of PVP matrix through the formation of reticulation points (i.e. nodes) via radical-radical coupling [Jin. 2007]. The former, reducing the chain mobility, should shift the T<sub>g</sub> towards higher temperatures where the degradation phenomena prevail making hardly observable T<sub>g</sub> (see Figure 43).



Figure 43. DSC curves of Heat Treated Electrospun Samples.

Figure 42b reports TGA curves recorded in the air on PVP\_tq, PVPSi\_HT, PVPSi\_5Ti\_HT, and PVPSi\_20Ti\_HT electrospun composites fiber mats. As can be seen, the oxidative thermal decomposition of pristine PVP occurred in three well-defined steps between 250 and 750 °C in agreement with the literature [Elishav 2018, Peniche 1993]. These studies suggest that besides the evacuation of water molecules physically trapped in the polymer matrix (first step), the thermal degradation of pristine PVP takes place mainly giving the corresponding side-chain monomer (i.e. pyrrolidone) and oligomers [Loría-Bastarrachea 2011]. From the profile of the PVP\_tq TGA curve the second step, which occurs in a narrow temperature range, can be related to the removal of the monomer while the decomposition of oligomers can be related to the

third step that occurs in a wide temperature range (Figure 42b). The main difference between the TGA curve of the pristine polymer and those of the composites concerns the second decomposition step that is shifted at higher temperatures for the composite materials indicating that both fillers increase the rigidity of the polymeric matrix. This is further confirmed by the analysis of TGA derivative profiles (DTG) shown in Figure 42c. The presence of silica and TiO<sub>2</sub>acac improves the thermal stability of PVP electrospun fiber mats leading to an increase of decomposition temperatures and final residual mass (~58 wt.% and ~62 wt.% for PVPSi\_5Ti\_HT and PVPSi\_20Ti\_HT respectively). Table 7.0 collects the corresponding TG data: T5% and T50% are the temperatures at which 5% and 50% weight loss are recorded; the residues at 800 °C and at the temperature ( $T_{max1}$ ) at which the weight loss rate reaches the maximum are also reported.

These results agree with the FTIR data previously discussed, as the presence of broad band at about  $3400 \text{ cm}^{-1}$  testify the presence of H-bonding that could be formed between Si-OH and Ti-OH with the C=O groups of the pyrrolidone ring. Moreover, the residual mass is close to those expected from the nominal composition of the samples, considering the significant mass loss of TiO<sub>2</sub>acac, confirming the high content of filler particles in the mats.

	T 5%	T 50%	T max1	<b>Residue at 800°C</b>
	(°C)	(°C)	(°C)	(%)
PVP_tq	60	356	319.6	0.6
PVPSi_HT	74.5	591	333	47
PVPSi_5Ti_HT	74.7	-	336.9	58
PVPSi_20Ti_HT	74.8	-	334.8	62

 Table 7.0 - TG data obtained in air atmosphere.

# 5.2.3. Morphological Analysis

In the electrospinning process, the addition of filler particles influences the morphological characteristics of electrospun fibers [Wachtler 2004]. For the preparation of composites, silica nanoparticles and TiO<sub>2</sub>acac microparticles were used. The silica nanoparticles were obtained by Stöber synthesis [Brinker 1990], showing a single distribution around  $80 \pm 20$  nm hydrodynamic radius (Figure 44) as evidenced by Dynamic Light Scattering (DLS) analysis. Conversely, the TiO<sub>2</sub>acac xereogel microparticles were obtained by a sol-gel route previously described [Sannino 2015, Aronne 2017, Koral 2020] and have a wide size distribution in the range of tens of  $\mu$ m, as shown by SEM micrographs in Figure 45.



Figure 44 – Hydrodynamic radius distribution obtained from DLS measurements for the solgel SiO<sub>2</sub>Np suspension in ethanol.



Figure 45 – a) Scanning electron microscopy (SEM) micrographs of TiO<sub>2</sub>acac xerogel, ground and sieved (90-120 μm fraction), b) particles size distributions.

Figure 46 and Figure 47 show SEM micrographs and fiber diameter distributions of electrospun PVPSi\_20Ti\_HT and PVPSi\_5Ti\_HT, respectively.



Figure 46. (a) Representative SEM image and fiber diameter histogram of PVPSi\_20Ti\_HT.
(b - c) SEM images of PVPSi\_20Ti\_HT at different magnifications showing the inclusion of SiO<sub>2</sub>NPs and TiO<sub>2</sub>acac confirming the formation of composite nanofiber mat. (d) EDX mapping of PVPSi\_20Ti\_HT showing presence and distribution of different elements.



**Figure 47.** (a) SEM micrographs and fiber diameter histogram of PVPSi\_5Ti\_HT. (b) SEM image of PVPSi\_5Ti\_HT at high magnification showing the inclusion of micro-filler (TiO<sub>2</sub>acac).

Both samples show the characteristic fibrous structures of electrospun materials. The fibers size distribution appears to be different compared to the bimodal distribution reported for PVPSi mats in Section 5.1.2.

Both ternary composites reveal a broad trimodal distribution, whose average diameters are reported in Table 8.0.

electrospun composite mats.

 Samples
 Fiber diameters (nm)

Table 8.0. Average fiber diameter for each class of diameters of

Samples	Fiber diameters (nm)
PVPSi	$330 \pm 30, 1600 \pm 600$
PVPSi_5Ti_HT	$350 \pm 60,680 \pm 95,1150 \pm 130$
PVPSi_20Ti_HT	$330 \pm 50,800 \pm 90,1500 \pm 350$

In particular, the first and third values are close to the previously reported diameter distribution (i.e.  $330 \pm 50$  nm and  $1.5 \pm 0.35 \ \mu$ m) for PVPSi electrospun mats (see Section 5.1.2). The PVPSi\_5Ti\_HT sample (Figure 47) is characterized by a similar broad distribution of fiber diameter. These differences in terms of size distribution between PVPSi, PVPSi\_20Ti\_HT, and PVPSi\_5Ti\_HT samples (Table 8.0) can be attributed to some change in operating conditions and nature, size as well as the amount of filler, since the variation in viscosity is known to affect the morphology of electrospun fibers [Lee 2018, Brettmann 2012].

The TiO<sub>2</sub>acac microparticles were successfully incorporated into the electrospun fibers, though their dimensions range is one-two orders of magnitude higher than the diameter of the fibers. This happens because of the Ti-OH groups which can interact with carbonyl groups of the PVP [Schlipf 2015]. As a consequence, the large TiO<sub>2</sub> particles appear firmly included in the fibers, rather than just physically trapped. Figures 46c, and 47b show that hybrid-titania microparticles are covered with silica nanoparticles also confirms the strong interaction between silanol and titanol groups. EDX mapping supports a uniform distribution of fillers (SiO<sub>2</sub>NPs and TiO<sub>2</sub>acac microparticles) throughout the fiber mat (Fig. 46d).

TEM micrographs of PVPSi\_20Ti\_HT evidenced that SiO<sub>2</sub> (Figure 48a) and relatively small TiO<sub>2</sub>acac (Figure 48b) particles are both arranged inside the nanofibers owing to the good interaction between -OH groups on the surface of oxide fillers and carbonyl groups of PVP [Gun'ko 2004]. TEM and SEM analysis confirm the successful production of electrospun fibres enclosing very large TiO<sub>2</sub>acac microparticles.

To the best of our knowledge, this is a new achievement in the field of electrospun composite materials and there are no previous works in the literature about electrospun polymer composites containing fillers of comparable size (i.e. up to  $90 \,\mu$ m).



**Figure 48.** TEM image of electrospun PVPSi\_20Ti\_HT at different magnification: (a) particular of SiO<sub>2</sub>NPs inside PVP fibers, (b) particular of TiO<sub>2</sub>acac microparticle covered by a thin layer of PVP and SiO<sub>2</sub>NPs.

#### **Zeta Potential results**

Surface Zeta potential of composite nanofiber mats were measured to evaluate the effect of TiO<sub>2</sub>acac on the surface chemistry.

The surface zeta ( $\zeta$ ) potential of the heat-treated samples was determined. In the case of hydrous oxides, the surface charge depends on the presence of the so-called "charge determining ions" (H<sup>+</sup> and OH<sup>-</sup>). This behavior is usually described as follows [Brinker 1990]:

$$M-OH + H^+ \to M-OH_2^+$$
<sup>(2)</sup>

$$M-OH + OH^{-} \rightarrow M-O^{-} + H_2O$$
(3)

the surface charge depends therefore on the acidity of the MOH group, that is on the nature of the M atom. The point of zero charge (PZC) is the pH at which the surface is not charged. At pH<PZC the surface is positively charged at pH>PZC it is negatively charged. Surface charge and potential increase with increasing distance from PZC.

The electrostatic potential drops in the EDL depending on its composition. The  $\zeta$ potential is the potential on the slip plane defined in the DLVO (Derjaguin, Landau,
Verwey Overbeek) theory; it depends on the surface charge and EDL composition.

Figure 49 shows how the ζ-potential changes with pH for PVPSi\_HT, PVPSi\_20Ti\_HT, and PVPSi\_5Ti\_HT. In the explored pH range, negative ζ-potential values were recorded in all cases, PVPSi\_20Ti\_HT one being shifted towards less negative values compared to PVPSi\_HT. These results may be explained considering the above FTIR and SEM analysis (Section 5.2.3.) that showing the presence of well-anchored titania particles exposed on the surface of electrospun composite fibers. The differences in ζ-potential observed between samples (Figure 49) can be ascribed to the different acidic characters of Si-OH and Ti-OH groups. As the reported point of zero charge (PZC) for silica is 2.5 [Brinker 1990], negative values of ζ-potential are expected for the PVPSi\_HT sample, the more negative the higher the pH as shown in Figure 50 and already reported [Csőgör 2003]. On the contrary, a PZC= 6.0 value is reported for titania [Brinker 1990]. Thus, the titania particles are expected to be positively charged or slightly negatively charged in the studied pH range. This is reflected in the marked shift toward higher values of the ζ-potential curve (on the top of the graph) of PVPSi\_20Ti\_HT. Compared to the PVPSi\_20Ti\_HT sample, the surface of the PVPSi\_20Ti\_HT.

PVPSi\_5Ti\_HT sample is similar to PVPSi one. Probably the lower TiO<sub>2</sub>acac content is not sufficient to produce substantial changes on the composite surface, whose electrical behavior remains dominated by silica.



**Figure 49.** ζ-potential of (a) PVPSi\_HT, (b) PVPSi\_5Ti\_HT and (c) PVPSi\_20Ti\_HT electrospun composite mats as a function of pH.

# **EPR** results

To get insight into the microstructural and electronic properties, the composite mats were analysed by Electron Paramagnetic Resonance (EPR) spectroscopy, a technique able to detect radicals and other species with unpaired electrons in solid or liquid samples. While the EPR spectrum of PVPSi\_HT (Figure 50) is practically silent, denoting the absence of such species, the samples containing TiO<sub>2</sub>acac present a composite signal, which seems to result from the overlapping of a single peak with an asymmetric signal. The intensity of these paramagnetic signals, increasing in the PVPSi\_20Ti\_HT sample, and their similarity to the spectrum of a TiO2acac xerogel treated at 200 °C [Imparato 2021] confirm that they are originated by the hybrid titania. The single peak, centred at g factor = 2.003, is probably due to radicals localized on the products of partial degradation of acac molecules, occurring during the treatment at 200 °C. Comparable, though more intense, EPR peaks were observed on TiO<sub>2</sub>acac annealed at 400 °C and were related to carbon-based species with a possible contribution from oxygen defects [Imparato 2020]. The asymmetric signal, comprising features at g-factor 2.025 and 2.009, can be attributed to the superoxide radical anion ( $O_2^{-}$ ) adsorbed on TiO<sub>2</sub> [Berger 2005]. This is a three-component signal, covered in part by the single peak. Superoxide anion is a reactive oxygen species involved in various oxidative processes, such as the degradation of pollutants or microorganisms [Hayyan 2016].

It is known that superoxide anion is spontaneously formed on the surface of TiO<sub>2</sub>acac xerogels after coming in contact with air and its regeneration with long-term persistence represents a peculiar feature of these hybrid oxides [Pirozzi 2020]. The evidence of superoxide radicals on ternary composite mats proves that even after thermal treatment and despite being prevalently embedded in the PVP fibers, TiO<sub>2</sub>acac particles retain their surface activity, hence the ability to generate these radicals and keep them stably adsorbed on the surface. The lower intensity of paramagnetic signals observed in case of PVPSi\_5Ti\_HT is due to the lower amount of TiO<sub>2</sub>acac, which is in agreement with FTIR and ζ-potential analysis. From EPR analysis it is clear that PVPSi\_20Ti\_HT is a potential candidate for pollutant degradation owing to its ability to produce a significantly higher number of superoxide radicals compared to PVPSi\_5Ti\_HT.

In summary, EPR results suggest PVPSi\_20Ti\_HT has the potential to be a promising composite material for pollutants degradation.



**Figure 50.** EPR spectra of heat-treated electrospun mats and TiO<sub>2</sub>-acetylacetonate dry gel particles recorded at room temperature, with g values indicated.

5.2.5. Methylene Blue Removal results

To assess the intrinsic decontamination ability of the ternary composite mat, we tested the removal from aqueous solution of MB as model pollutant in the dark. Considering  $\zeta$ -potential and EPR results, PVPSi\_20Ti\_HT was selected for the decontamination experiments along with PVPSi\_HT as the reference. PVPSi\_20Ti\_HT showed a higher initial MB removal rate (0.25 h-1) compared to PVPSi\_HT (0.15 h-1) (Fig. 51). This eventually led to higher MB removal efficiency after 6 h (42%) as compared to only 35% in case of PVPSi\_HT (Fig. 51).

Adsorption is expected to be the prevalent mechanism involved in the removal of MB, as testified by the blue coloration of the composite mats after the test. Silica particles present in both samples can show significant adsorption capacity toward cationic dyes such as MB [Parida 2021]. The adsorption on PVPSi\_HT is favored by its negative surface charge evidenced by  $\zeta$ -potential measurements (Fig. 7). Despite of its higher  $\zeta$ -potential, the better performance shown by PVPSi\_20Ti\_HT can be explained by the contribution of TiO2acac, promoting oxidative degradation of MB through adsorbed superoxide radicals (Section 3.3). Interestingly, such degradation mediated by the reactive oxygen radicals does not require light irradiation [Pirozzi 2020] which makes the implementation of such materials convenient in terms of costs and operative conditions.

The MB concentration decay tends to reach an equilibrium in both samples. To better understand the phenomena involved in the water decontamination, decay curves were fitted with different kinetic models. The most accurate analytical description of the trends was obtained by a pseudo-first order model proposed by Lagergren for adsorption analysis (Eq. 4) [Lin 2007] and widely used also for the modelling of photodegradation processes [Hu 2012, Fu 2020], where C is the MB concentration at time t, C<sub>0</sub> is the initial MB concentration, k is the rate constant (h<sup>-1</sup>), ms is the sample loading (g L<sup>-1</sup>), q<sub>e</sub> is the amount of dye removed at equilibrium (mg g<sup>-1</sup>) and A = (m<sub>s</sub> q<sub>e</sub> /C<sub>0</sub>).

$$C/C_0 = (1-A) + Ae^{-kt}$$
(4)

The resulting kinetic parameters are reported in Table 8.0. The pseudo-first order function gives a good fitting of the MB concentration decay in the presence of PVPSi\_20Ti\_HT, which does not rule out the hypothesis of an adsorption-degradation mechanism, with the two simultaneous processes contributing to the removal efficiency. For PVPSi\_HT the fitting is slightly less satisfactory, as the concentration profile seems
to be composed of two ranges with different slopes, maybe due to the saturation of the fraction of  $SiO_2NPs$  exposed on the fibers surface followed by a slower adsorption on less accessible particles. The calculated rates show that the process is faster in presence of the ternary sample (PVPSi\_20Ti\_HT, Table 9.0).

**Table 9.0**. Fitting parameters for the MB concentration decay in presence ofthe composite mats, by pseudo-first order equation (Eq. 4).

Sample	А	k (h <sup>-1</sup> )	R <sup>2</sup>	$q_e (mg g^{-1})$
PVPSi_HT	$0.40\pm0.03$	$0.43\pm0.08$	0.977	3.97
PVPSi_20Ti_HT	$0.425\pm0.006$	$0.69\pm0.03$	0.998	4.25

To confirm the differences in the behavior of the two materials, PVPSi\_20Ti\_HT was reused under the same conditions, after rinsing in water. Noticeably, PVPSi\_20Ti\_HT demonstrated a higher activity than PVPSi\_HT also in the second run (Figure 51). These experimental results highlight a relevant degradation effect induced by TiO<sub>2</sub>acac. In view of the above, this preliminary study opens perspectives for the application of these ternary composite mats in water treatment.



**Figure 51**. Relative MB concentration in solution in the presence of electrospun samples in dark condition ( $C0 = 10 \text{ mg L}^{-1}$ ). PVPSi\_HT: first run (a), second run (b);

PVPSi\_20Ti\_HT: first run (c), second run (d).

## **6.0** Conclusion

The goal of this PhD work was to show the use of sol-gel chemistry in the development of some innovative electrospun composite materials for relevant aircraft and environmental applications.

Sol-gel chemistry is a "bottom-up" synthesis that allows to produce films, nano/micro particles, fibers, gels and bulk materials both glassy and crystalline. Through the use of the very well-known hydrolysis and polycondensation reactions, silicatic materials can be obtained from the Si precursor tetraethoxysilane (TEOS). In particular, the "Stöber" method exploits an alkaline environment to synthetize monodisperse silica particles with sizes from a few nanometers till micron. Therefore, the sol-gel chemistry can be a crucial tool to find the solution for several industrial applications which require the implementation of nanotechnology to overcome some limitations of polymer materials (e.g. low resistance to organic solvents, thermal instability, low mechanical properties, easy flammability etc.).

The development of new nanocomposite materials continues to be a main interest in materials science. Among the methods used to fabricate nanomaterials, electrospinning is a simple and cost-effective technique which relies on repulsive electrostatic forces to produce nanofibers from a viscoelastic polymer solution. Electrospun nanofibers have

been used in a variety of applications, ranging from extractive sorbents and membranes to drug delivery and tissue scaffolds. Electrospinning typically utilizes a high molecular weight polymer to provide the chain entanglement required to keep the polymeric jet intact during the spinning process. As a result, the versatility of electrospun polymer nanofibers is restricted due to the limited functionalities that pure polymer nanofibers offer. Thus, various polymer blends and polymer/inorganic mixtures have been developed into multifunctional polymer/inorganic composite nanofibers which vastly expand the variety of functionalities capable of being produced via electrospinning.

For the reasons listed above, the aim of this PhD project was to simultaneously exploit the numerous advantages of sol-gel chemistry and of electrospinning process, in order to produce novel-PVP based composite materials employed in several applications such as aircraft vibro-acoustic membranes or water pollutants absorbers.

In the first part of this PhD project, new electrospun PVP\_SiO<sub>2</sub>Np material that preserve the good acoustical properties of pure PVPs was successfully obtained using an eco-friendly electrospinning process, based on ethanol suspension of PVP and sol-gel silica Np.

On the basis of characterizations results, it was concluded that PVP\_SiO<sub>2</sub>Np electrospun composites containing 67% of sol-gel silica are more suitable for sound adsorption properties, in the lower frequency range, as compared to other materials (e.g. glass wool) currently used as fuselage coating in aircrafts.

When plotting the acoustical absorption coefficient as a function of frequency, bell shaped curves were recorded, whose maximum (where the coefficient is greater than 0.9) shifts to lower frequencies the greater the mass of piled disks. The acoustic behavior can be, therefore, continuously tuned by changing the mass of the blanket.

A thermal cross-link treatment was defined that gave mats do possess excellent water resistance thus improving the great solubility of raw PVP. Furthermore, the presence of incorporated sol-gel silica Np inside the fibers dimensionally stabilizes the mats upon thermal treatments avoiding the fibers shrinkage.

This study, therefore, proves that electrospun PVP\_SiO<sub>2</sub>Np has passed the fire tests (Vertical Bunsen Burner and Smoke Density) that are mandatory in aerospace engineering field. The self- extinguishing is possible only in combination with silica

particles. Preliminary investigation of thermal conductivity through Differential Scanning Calorimetry (DSC) shows that they can also be used for thermal insulation.

The experimental results indicate that the achievements can be ascribed to the chemical nature of PVP. It is a polymeric lactam with a side polar group that may be easily released by a thermo oxidative process. The side polar groups of the PVP allow to use ethanol for electrospinning and ensure a good dispersion of silica gel particles.

This innovative material seems to be the most performing as regard its proprieties and safeness, it is absolutely the most promising in compliance with the regulations in aeronautics, even though its usages could be extended to many other fields.

Taking into account the intensity of research and the development in manufacturing processes, the study of new sound-absorbing materials will expand quickly over the next few years. In the future it would be useful to find a method to improve mechanical proprieties of the PVP\_SiO<sub>2</sub> mats, an important characteristic that unfortunately still remains unsolved. The developed PVP\_SiO<sub>2</sub> mats production would require a scale-up process, in order to accelerate research, experimentation, patenting and hopefully marketing.

In the second part of this work, novel ternary electrospun composite mats  $PVP/SiO_2Np/TiO_2acac$ , enclosing very large  $TiO_2acac$  microparticles (i.e. up to 90  $\mu$ m), were successfully obtained by an eco-friendly electrospinning technique. To the best of our knowledge, the production of composites based on polymer fibers with fillers in this size range is a new achievement in the field of electrospun materials.

The thermal treatment at 200 °C, inducing cross-linking and initial oxidation of the polymer chains, was effective to provide stability and water resistance to the composite mats. The effect of TiO<sub>2</sub>acac concentration on the properties of electrospun fibers was evaluated. TiO<sub>2</sub>acac particles appear well dispersed in the polymeric matrix and the Ti-acac complexes were retained after thermal treatment. The results of DSC confirmed that hybrid titania influences PVP polymer thermal behavior slightly raising its Tg. TGA analysis showed improved thermal stability of ternary composites, with increasing hybrid titania content. Morphological analysis displayed a trimodal distribution of fiber diameter for composite samples and evidence that both SiO<sub>2</sub> nanoparticles and TiO<sub>2</sub>acac microparticles are arranged inside the nanofibers, owing to the stable interaction which occurs between -OH groups on the surface of inorganic fillers and carbonyl groups of PVP. The surface zeta potential may be tuned by changing the titania particles content.

EPR spectra show the presence of stably adsorbed superoxide radicals generated by TiO<sub>2</sub>acac particles. Superoxide anion is a reactive oxygen species involved in various oxidative processes, such as the degradation of pollutants.

The ternary composite mat showed enhanced activity in the removal of MB in absence of light irradiation, confirming the importance of the degradation effect induced by the presence of high content of hybrid TiO<sub>2</sub>acac in the PVP fibers. This result opens perspectives for the application of these ternary composites in water treatment or remediation.

The data suggest that a synergistic effect between TiO<sub>2</sub>acac microparticles, SiO<sub>2</sub>Np and PVP is a prerequisite for efficient adsorption/degradation activity. Furthermore, these ternary electrospun mats can be interesting as novel materials in various applications such as filtration, catalysis, and antimicrobial activity. However, future research would be focused on the development and functionalization of the PVP/SiO<sub>2</sub>Np/TiO<sub>2</sub>acac fiber mats to improve the properties and extend their application fields.

Finally, in this PhD thesis it has been demonstrated that the use of sol-gel materials within electrospun polymer fibers leads to the production of composites that simultaneously exploit the advantages of the sol-gel methodology and the ease of manufacture of the electrospinning process. The addition of silica particles made the fibrous polymer structure resistant to water and fire, making it suitable for aerospace use, while the further addition of hybrid titania made the material a promising absorber of aqueous pollutants.

## References

- Adams, R. D. (Ed.). (2005). Adhesive bonding: science, technology and applications. Elsevier.
- Agarwal, S., Greiner, A., & Wendorff, J. H. (2013). Functional materials by electrospinning of polymers. Progress in Polymer Science, 38(6), 963-991.
- Al Rai, A., Stojanovska, E., Akgul, Y., Khan, M. M., Kilic, A., & Yilmaz, S. (2021). Fabrication
  of co-PVDF/modacrylic/SiO2 nanofibrous membrane: Composite separator for safe and high
  performance lithium-ion batteries. Journal of Applied Polymer Science, 138(7), 49835.
- Al-Harbi, L. M., Kosa, S. A., Baloch, M. K., Bhatti, Q. A., & El-Mossalamy, E. S. E. B. H. (2016). Adsorption of polyvinylpyrrolidone over the silica surface: as affected by pretreatment of adsorbent and molar mass of polymer adsorbate. International Journal of Polymer Science, 2016.
- Andrady, A. (2008). Science and Technology of Polymer Nanofibers; Wiley: Hoboken, New Jersey.
- Arenas, J.P., Crocker, M.J. (2010). Recent Trends in Porous Sound-Absorbing Materials. Sound Vib. 44, 12–18.
- Aronne, A., Fantauzzi, M., Imparato, C., Atzei, D., De Stefano, L., D'Errico, G., ... & Rossi, A. (2017). Electronic properties of TiO 2-based materials characterized by high Ti 3+ self-doping and low recombination rate of electron–hole pairs. Rsc Advances, 7(4), 2373-2381.
- Aronne, A., Marenna, E., Califano, V., Fanelli, E., Pernice, P., Trifuoggi, M., & Vergara, A. (2007). Sol–gel synthesis and structural characterization of niobium-silicon mixed-oxide nanocomposites. Journal of sol-gel science and technology, 43(2), 193-204.

- Avossa, J., Branda, F., Marulo, F., Petrone, G., Guido, S., Tomaiuolo, G., & Costantini, A. (2018). Light electrospun polyvinylpyrrolidone blanket for low frequencies sound absorption. Chinese Journal of Polymer Science, 36(12), 1368-1374.
- Baiju, K.V., Periyat, P., Wunderlich, W., Pillai, P.K., Mukundan, P., Warrier, K.G.K. (2007). Enhanced photoactivity of neodymium doped mesoporous titania synthesized through aqueous sol–gel method. J. Sol-Gel Sci. Technol. 43(3), 283–290.
- Baji, A., Agarwal, K., & Oopath, S. V. (2020). Emerging developments in the use of electrospun fibers and membranes for protective clothing applications. Polymers, 12(2), 492.
- Barakat, N. A., Khil, M. S., Sheikh, F. A., & Kim, H. Y. (2008). Synthesis and optical properties
  of two cobalt oxides (CoO and Co3O4) nanofibers produced by electrospinning process. The
  Journal of Physical Chemistry C, 112(32), 12225-12233.
- Barber, A. (1992). Handbook of Noise and Vibration Control, 6th ed.; Elsevier Advanced Technology: Oxford, UK, ISBN 978-1-85617-079-6.
- Berardi, U., & Iannace, G. (2015). Acoustic characterization of natural fibers for sound absorption applications. Building and Environment, 94, 840-852.
- Berg, J. C. (2010). An introduction to interfaces & colloids: the bridge to nanoscience. World Scientific.
- Berger, T., Sterrer, M., Diwald, O., Knözinger, E., Panayotov, D., Thompson, T. L., & Yates, J. T. (2005). Light-induced charge separation in anatase TiO2 particles. The Journal of Physical Chemistry B, 109(13), 6061-6068.
- Bhardwaj, N., Kundu, C. (2010). Electrospinning: A fascinating fiber fabrication technique. Biotechnology Advances, 28, 325-347.
- Bifulco, A., Parida, D., Salmeia, K. A., Nazir, R., Lehner, S., Stämpfli, R., ... & Gaan, S. (2020). Fire and mechanical properties of DGEBA-based epoxy resin cured with a cycloaliphatic hardener: Combined action of silica, melamine and DOPO-derivative. Materials & Design, 193, 108862.
- Boday, D. J., Wertz, J. T., & Kuczynski, J. P. (2015). Functionalization of silica nanoparticles for corrosion prevention of underlying metal. Nanomaterials, polymers and devices: materials functionalization and device fabrication, 1st edn. Wiley, Hoboken, 121-140.
- Bogatyrev, V. M., Borisenko, N. V., & Pokrovskii, V. A. (2001). Thermal degradation of polyvinylpyrrolidone on the surface of pyrogenic silica. Russian Journal of Applied Chemistry, 74(5), 839-844.
- Bognitzki, M., Frese, T., Steinhart, M., Greiner, A., Wendorff, J. H. (2001). Preparation of fibers with nanoscaled morphologies: electrospinning of polymer blends. Polymer Engineering and Science, 41, 982-989.
- Bogush, G. H., & Zukoski Iv, C. F. (1991). Studies of the kinetics of the precipitation of uniform silica particles through the hydrolysis and condensation of silicon alkoxides. Journal of Colloid and Interface Science, 142(1), 1-18.
- Bogush, G. H., Tracy, M. A., & Zukoski Iv, C. F. (1988). Preparation of monodisperse silica particles: control of size and mass fraction. Journal of non-crystalline solids, 104(1), 95-106.

- Boissière, C., Larbot, A., Bourgaux, C., Prouzet, E., & Bunton, C. A. (2001). A study of the assembly mechanism of the mesoporous MSU-X silica two-step synthesis. Chemistry of materials, 13(10), 3580-3586.
- Boissiere, C., Larbot, A., van der Lee, A., Kooyman, P. J., & Prouzet, E. (2000). A new synthesis of mesoporous MSU-X silica controlled by a two-step pathway. Chemistry of materials, 12(10), 2902-2913.
- Boissière, C., Van Der Lee, A., El Mansouri, A., Larbot, A., & Prouzet, E. (1999). A double step synthesis of mesoporous micrometric spherical MSU-X silica particles. Chemical Communications, (20), 2047-2048.
- Brame, J., Long, M., Li, Q., & Alvarez, P. (2014). Trading oxidation power for efficiency: differential inhibition of photo-generated hydroxyl radicals versus singlet oxygen. water research, 60, 259-266.
- Brettmann, B. K., Tsang, S., Forward, K. M., Rutledge, G. C., Myerson, A. S., & Trout, B. L. (2012). Free surface electrospinning of fibers containing microparticles. Langmuir, 28(25), 9714-9721.
- Brinker, C. J., & Scherer, G. W. (1990). Sol-gel science: the physics and chemistry of sol-gel processing. Academic press.
- Buchalska, M., Kobielusz, M., Matuszek, A., Pacia, M., Wojtyła, S., & Macyk, W. (2015). On oxygen activation at rutile-and anatase-TiO2. ACS Catalysis, 5(12), 7424-7431.
- Cademartiri, R., Brook, M. A., Pelton, R., & Brennan, J. D. (2009). Macroporous silica using a "sticky" Stöber process. Journal of Materials Chemistry, 19(11), 1583-1592.
- Carbonaro, S., Sugihara, M. N., & Strathmann, T. J. (2013). Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: activity, inhibition, and deactivation of TiO2 photocatalysts in wastewater effluent. Applied Catalysis B: Environmental, 129, 1-12.
- Carp, O., Huisman, C. L., & Reller, A. (2004). Photoinduced reactivity of titanium dioxide. Progress in solid state chemistry, 32(1-2), 33-177.
- Carrus, M., Fantauzzi, M., Riboni, F., Makosch, M., Rossi, A., Selli, E., & Van Bokhoven, J. A. (2016). Increased conversion and selectivity of 4-nitrostyrene hydrogenation to 4-aminostyrene on Pt nanoparticles supported on titanium-tungsten mixed oxides. Applied Catalysis A: General, 519, 130-138.
- Chen, X., & Mao, S. S. (2007). Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chemical reviews, 107(7), 2891-2959.
- Chen, Y. Z., Zhang, Z. P., Yu, J., & Guo, Z. X. (2009). Poly (methyl methacrylate)/silica nanocomposite fibers by electrospinning. Journal of Polymer Science Part B: Polymer Physics, 47(12), 1211-1218.
- Cheng, C., Wu, J., Xiao, Y., Chen, Y., Fan, L., Huang, M., ... & Yue, G. (2011). Polyvinyl pyrrolidone aided preparation of TiO2 films used in flexible dye-sensitized solar cells. Electrochimica acta, 56(21), 7256-7260.
- Choi, S. S., Lee, S. G., Im, S. S., Kim, S. H., & Joo, Y. L. (2003). Silica nanofibers from electrospinning/sol-gel process. Journal of Materials Science Letters, 22(12), 891-893.

- Chung, J. Y., & Blaser, D. A. (1980). Transfer function method of measuring in-duct acoustic properties. I. Theory. The Journal of the Acoustical Society of America, 68(3), 907-913.
- Crocker, M. (1997). Handbook of acoustics, Wiley, New York.
- Crocker, M.J. (2007). Handbook of Noise and Vibration Control; John Wiley & Sons: Hoboken, NJ, USA, ISBN 978-0-471-39599-7.
- Csőgör, Z., Nacken, M., Sameti, M., Lehr, C. M., & Schmidt, H. (2003). Modified silica particles for gene delivery. Materials Science and Engineering: C, 23(1-2), 93-97.
- Danks, A. E., Hall, S. R., & Schnepp, Z. J. M. H. (2016). The evolution of 'sol-gel'chemistry as a technique for materials synthesis. Materials Horizons, 3(2), 91-112.
- De Vrieze, S., Van Camp, T., Nelvig, A., Hagström, B., Westbroek, P., & De Clerck, K. (2009). The effect of temperature and humidity on electrospinning. Journal of materials science, 44(5), 1357-1362.
- Demir, M. M., Yilgor, I., Yilgor, E., Erman, B. (2002). Electrospinning of polyurethane fibers. Polymer, 43, 3303-3309.
- Desai, K., Kit, K., Li, J., & Zivanovic, S. (2008). Morphological and surface properties of electrospun chitosan nanofibers. Biomacromolecules, 9(3), 1000-1006.
- Dhand, V., Mittal, G., Rhee, K. Y., Park, S. J., & Hui, D. (2015). A short review on basalt fiber reinforced polymer composites. Composites Part B: Engineering, 73, 166-180.
- Diaz-Acosta, I., Baker, J., Hinton, J. F., & Pulay, P. (2003). Calculated and experimental geometries and infrared spectra of metal tris-acetylacetonates: vibrational spectroscopy as a probe of molecular structure for ionic complexes. Part II. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59(2), 363-377.
- Ding, X., Zhao, J., Liu, Y., Zhang, H., & Wang, Z. (2004). Silica nanoparticles encapsulated by polystyrene via surface grafting and in situ emulsion polymerization. Materials Letters, 58(25), 3126-3130.
- Doeuff, S., Henry, M., Sanchez, C., & Livage, J. (1987). Hydrolysis of titanium alkoxides: modification of the molecular precursor by acetic acid. Journal of Non-crystalline solids, 89(1-2), 206-216.
- Dong, H., Zeng, G., Tang, L., Fan, C., Zhang, C., He, X., & He, Y. (2015). An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. Water research, 79, 128-146.
- Drašar, P. (2016). Levy David, Zayat Marcos (ed.): The Sol-Gel Handbook: Synthesis, Characterization and Applications. Chemické listy, 110(3), 229-230.
- Eatwell, G., & Busch, R. (2007). U.S. Patent Application No. 11/484,065.
- Elishav, O., Beilin, V., Rozent, O., Shter, G. E., & Grader, G. S. (2018). Thermal shrinkage of electrospun PVP nanofibers. Journal of Polymer Science Part B: Polymer Physics, 56(3), 248-254.
- Engel, Z. (2014). Notes on Sound Absorption Technology, K.U. INGARD. Arch. Acoust. 21, 115–117.

- Fan, C., Chen, C., Wang, J., Fu, X., Ren, Z., Qian, G., & Wang, Z. (2015). Black hydroxylated titanium dioxide prepared via ultrasonication with enhanced photocatalytic activity. Scientific reports, 5(1), 1-10.
- Formhals, A. (1934). Process and apparatus for preparing artificial threads Us patent 1975504.
- Fu W, Lu D-L, Yao H, Yuan S, Wang W, Gong M, et al. Simultaneous roxarsone photocatalytic degradation and arsenic adsorption removal by TiO2/FeOOH hybrid. Environmental Science & Pollution Research. 2020;27(15).
- Fujishima, A., & Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. nature, 238(5358), 37-38.
- Fujishima, A., Zhang, X., & Tryk, D. A. (2008). TiO2 photocatalysis and related surface phenomena. Surface science reports, 63(12), 515-582.
- Ge, L., Sethi, S., Ci, L., Ajayan, P. M., Dhinojwala, A. (2007). Carbon nanotube-basedsynthetic gecko tapes. Proceedings of the National Academy of Science. 104, 10792-10795.
- Ghobadi, S., Sadighikia, S., Papila, M., Cebeci, F. Ç., & Gürsel, S. A. (2015). Graphenereinforced poly (vinyl alcohol) electrospun fibers as building blocks for high performance nanocomposites. RSC advances, 5(103), 85009-85018.
- Giannakis, S., Liu, S., Carratalà, A., Rtimi, S., Amiri, M. T., Bensimon, M., & Pulgarin, C. (2017). Iron oxide-mediated semiconductor photocatalysis vs. heterogeneous photo-Fenton treatment of viruses in wastewater. Impact of the oxide particle size. Journal of hazardous materials, 339, 223-231.
- Goines, L.; Hagler, L.C.S.M. (2007). Noise Pollution: A Modern Plague. South. Med. J. 100, 287–394.
- Gun'ko, V. M., Voronin, E. F., Zarko, V. I., Goncharuk, E. V., Turov, V. V., Pakhovchishin, S. V., ... & Chuiko, A. A. (2004). Interaction of poly (vinyl pyrrolidone) with fumed silica in dry and wet powders and aqueous suspensions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 233(1-3), 63-78.
- Guo, A., Liu, J., Dong, X., & Liu, M. (2013). Preparation of porous silica ceramics from silica spinning solution and introduced silica particles by electrospinning. Materials Letters, 95, 74-77..
- Haaf, F., Sanner, A., Straub, F. (1985). Polymers of N-vinyplyrrolidone: synthesis, characterization and used. Polymer Journal, 17, 143-152.
- Haghi, A. K., & Akbari, M. (2007). Trends in electrospinning of natural nanofibers. physica status solidi (a), 204(6), 1830-1834.
- Haider, A., Haider, S., & Kang, I. K. (2018). A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology. Arabian Journal of Chemistry, 11(8), 1165-1188.
- Haitao N., Tong L. (2012). Fiber Generators in Needleless Electrospinning, Journal of Nanomaterials,13.
- Harris, C.M. (1991). Handbook of Acoustical Measurements and Noise Control, 3rd ed.; McGraw Hill: New York, NY, USA, ISBN 978-0-07-026868-5.

- Hayyan, M., Hashim, M. A., & AlNashef, I. M. (2016). Superoxide ion: generation and chemical implications. Chemical reviews, 116(5), 3029-3085.
- He, T., Zhou, Z., Xu, W., Ren, F., Ma, H., & Wang, J. (2009). Preparation and photocatalysis of TiO2–fluoropolymer electrospun fiber nanocomposites. Polymer, 50(13), 3031-3036.
- Horner, A. (2000). Aircraft materials fire test handbook (No. DOT/FAA/AR-00/12). United States. Federal Aviation Administration.
- Hu A, Zhang X, Luong D, Oakes KD, Servos MR, Liang R, et al. Adsorption and photocatalytic degradation kinetics of pharmaceuticals by TiO 2 nanowires during water treatment. Waste and Biomass Valorization. 2012;3(4):443-9.
- Hu, L., Flanders, P. M., Miller, P. L., & Strathmann, T. J. (2007). Oxidation of sulfamethoxazole and related antimicrobial agents by TiO2 photocatalysis. Water research, 41(12), 2612-2626.
- Hu, M., Yu, D., & Wei, J. (2007). Thermal conductivity determination of small polymer samples by differential scanning calorimetry. Polymer testing, 26(3), 333-337.
- Huang, A., Wang, N., Lei, M., Zhu, L., Zhang, Y., Lin, Z., ... & Tang, H. (2013). Efficient oxidative debromination of decabromodiphenyl ether by TiO2-mediated photocatalysis in aqueous environment. Environmental science & technology, 47(1), 518-525.
- Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites science and technology, 63(15), 2223-2253.
- Hüsing, N., Schubert, U., Misof, K., & Fratzl, P. (1998). Formation and Structure of Porous Gel Networks from Si (OMe) 4 in the Presence of A (CH2) n Si (OR) 3 (A= Functional Group). Chemistry of materials, 10(10), 3024-3032.
- Iannace, G. (2014). Sound absorption of materials obtained from the shredding of worn tyres. Building acoustics, 21(4), 277-286.
- Iannace, G., Ciaburro, G., & Trematerra, A. (2019). Fault diagnosis for UAV blades using artificial neural network. Robotics, 8(3), 59.
- Iannace, G., Ciaburro, G., & Trematerra, A. (2020). Modelling sound absorption properties of broom fibers using artificial neural networks. Applied Acoustics, 163, 107239.
- Iler, K. R. (1979). The chemistry of silica. Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica
- Im, J. S., Park, S. J., Kim, T. J., Kim, Y. H., & Lee, Y. S. (2008). The study of controlling pore size on electrospun carbon nanofibers for hydrogen adsorption. Journal of colloid and interface science, 318(1), 42-49.
- Imparato, C., Iervolino, G., Fantauzzi, M., Koral, C., Macyk, W., Kobielusz, M., ... & Aronne, A. (2020). Photocatalytic hydrogen evolution by co-catalyst-free TiO 2/C bulk heterostructures synthesized under mild conditions. RSC Advances, 10(21), 12519-12534.
- Imparato, C., Passaro, J., Bifulco, A., Branda, F., Pirozzi, D., & Aronne, A. (2021). Development of Hybrid Titanium Oxide-based Systems for the Surface Stabilization of Reactive Oxygen Radicals. Chemical Engineering Transactions, 84, 139-144.

- Jafry, H. R., Liga, M. V., Li, Q., & Barron, A. R. (2011). Simple route to enhanced photocatalytic activity of P25 titanium dioxide nanoparticles by silica addition. Environmental science & technology, 45(4), 1563-1568.
- Jang, I., Song, K., Park, J. H., Kim, M., Kim, D. W., & Oh, S. G. (2013). Effect of PVP molecular weight on the formation of Ag nanoparticles on echinoid-like TiO2. Materials Letters, 96, 214-217.
- Ji, L., & Zhang, X. (2008b). Ultrafine polyacrylonitrile/silica composite fibers via electrospinning. Materials Letters, 62(14), 2161-2164.
- Ji, L., Saquing, C., Khan, S. A., & Zhang, X. (2008a). Preparation and characterization of silica nanoparticulate–polyacrylonitrile composite and porous nanofibers. Nanotechnology, 19(8), 085605.
- Jin, M., Zhang, X., Nishimoto, S., Liu, Z., Tryk, D. A., Murakami, T., & Fujishima, A. (2007). Large-scale fabrication of Ag nanoparticles in PVP nanofibres and net-like silver nanofibre films by electrospinning. Nanotechnology, 18(7), 075605.
- Ju, H., Zhang, X., & Wang, J. (2011). Biosensors based on sol-gel nanoparticle matrices. In NanoBiosensing (pp. 305-332). Springer, New York, NY.
- Kanehata, M., Ding, B., & Shiratori, S. (2007). Nanoporous ultra-high specific surface inorganic fibres. Nanotechnology, 18(31), 315602.
- Kätzel, U., Vorbau, M., Stintz, M., Gottschalk-Gaudig, T., & Barthel, H. (2008). Dynamic light scattering for the characterization of polydisperse fractal systems: II. Relation between structure and DLS results. Particle & Particle Systems Characterization, 25(1), 19-30.
- Kessler, V. G. (2009). The chemistry behind the sol-gel synthesis of complex oxide nanoparticles for bio-imaging applications. Journal of sol-gel science and technology, 51(3), 264-271.
- Kessler, V. G., Spijksma, G. I., Seisenbaeva, G. A., Håkansson, S., Blank, D. H., & Bouwmeester, H. J. (2006). New insight in the role of modifying ligands in the sol-gel processing of metal alkoxide precursors: A possibility to approach new classes of materials. Journal of solgel science and technology, 40(2), 163-179.
- Khan, W. (2010). Nanomaterials fabrication and characterization for various applications. Ph.D. dissertation, Wichita State Univ., KS, USA.
- Khan, W. S., Asmatulu, R., & Yildirim, M. B. (2012). Acoustical properties of electrospun fibers for aircraft interior noise reduction. Journal of Aerospace Engineering, 25(3), 376-382.
- Kickelbick, G. (2007). Introduction to hybrid materials. Hybrid materials, 1, 2.
- Kim, Y. J., Ahn, C. H., Lee, M. B., & Choi, M. S. (2011). Characteristics of electrospun PVDF/SiO2 composite nanofiber membranes as polymer electrolyte. Materials Chemistry and Physics, 127(1-2), 137-142.
- Kolbe, G. (1956). Das komplexchemische verhalten der kieselsaure." phdthesis. Friedrich-Schiller-Universitat Jena.

- Kongkhlang, T., Tashiro, K., Kotaki, M., & Chirachanchai, S. (2008). Electrospinning as a new technique to control the crystal morphology and molecular orientation of polyoxymethylene nanofibers. Journal of the American Chemical Society, 130(46), 15460-15466.
- Koombhongse, S., Liu, W., & Reneker, D. H. (2001). Flat polymer ribbons and other shapes by electrospinning. Journal of Polymer Science Part B: Polymer Physics, 39(21), 2598-2606.
- Koral, C., Fantauzzi, M., Imparato, C., Papari, G. P., Silvestri, B., Aronne, A., ... & Rossi, A. (2020). Defects in the Amorphous–Crystalline Evolution of Gel-Derived TiO2. The Journal of Physical Chemistry C, 124(43), 23773-23783.
- Koruk, H. (2014). An assessment of the performance of impedance tube method. Noise Control Engineering Journal, 62(4), 264-274.
- Kruk, M., Jaroniec, M., & Sayari, A. (1999). Surface heterogeneity analysis of MCM-41 metallosilicates by using nitrogen adsorption data. Langmuir, 15(18), 5683-5688.
- Kuchi, C., Harish, G. S., & Reddy, P. S. (2018). Effect of polymer concentration, needle diameter and annealing temperature on TiO2-PVP composite nanofibers synthesized by electrospinning technique. Ceramics International, 44(5), 5266-5272.
- Kumar, S. G., & Rao, K. K. (2014). Polymorphic phase transition among the titania crystal structures using a solution-based approach: from precursor chemistry to nucleation process. Nanoscale, 6(20), 11574-11632.
- LaMer, V. K., & Dinegar, R. H. (1950). Theory, production and mechanism of formation of monodispersed hydrosols. Journal of the American Chemical Society, 72(11), 4847-4854.
- Langfeldt, F., & Gleine, W. (2019). Improved sound transmission loss of glass wool with acoustic metamaterials. Proc 26th ICSV, 7-11
- Lanotte, L., Bilotti, C., Sabetta, L., Tomaiuolo, G., & Guido, S. (2013). Dispersion of sepiolite rods in nanofibers by electrospinning. Polymer, 54(4), 1295-1297.
- Leaustic, A., Babonneau, F., & Livage, J. (1989). Structural investigation of the hydrolysiscondensation process of titanium alkoxides Ti (OR) 4 (OR= OPr-iso, OEt) modified by acetylacetone. 1. Study of the alkoxide modification. Chemistry of Materials, 1(2), 240-247..
- Lee, C. G., Javed, H., Zhang, D., Kim, J. H., Westerhoff, P., Li, Q., & Alvarez, P. J. (2018). Porous electrospun fibers embedding TiO2 for adsorption and photocatalytic degradation of water pollutants. Environmental science & technology, 52(7), 4285-4293.
- Lee, J., Hong, S., Mackeyev, Y., Lee, C., Chung, E., Wilson, L. J., ... & Alvarez, P. J. (2011). Photosensitized oxidation of emerging organic pollutants by tetrakis C60 aminofullerenederivatized silica under visible light irradiation. Environmental science & technology, 45(24), 10598-10604.
- Lee, S. Y., & Park, S. J. (2014). Isothermal exfoliation of graphene oxide by a new carbon dioxide pressure swing method. Carbon, 68, 112-117.
- Li, Y., Ding, B., Sun, G., Ke, T., Chen, J., Al-Deyab, S. S., & Yu, J. (2014). Solid-phase pinkto-purple chromatic strips utilizing gold probes and nanofibrous membranes combined system for lead (II) assaying. Sensors and Actuators B: Chemical, 204, 673-681.

- Lim, J. M., Moon, J. H., Yi, G. R., Heo, C. J., & Yang, S. M. (2006). Fabrication of onedimensional colloidal assemblies from electrospun nanofibers. Langmuir, 22(8), 3445-3449.
- Lim, J., Kim, H., Alvarez, P. J., Lee, J., & Choi, W. (2016). Visible light sensitized production of hydroxyl radicals using fullerol as an electron-transfer mediator. Environmental science & technology, 50(19), 10545-10553.
- Lin JX, Zhan SL, Fang MH, Qian XQ. The adsorption of dyes from aqueous solution using diatomite. Journal of Porous Materials. 2007;14(4):449-55.
- Liu, H., Wang, D., Zhao, N., Ma, J., Gong, J., Yang, S., Xu, J. (2014). Application of electrospinning fibres on sound absorption in low and medium frequency range. Mater. Res. Innov. 18, 888–891.
- Liu, J., Qiao, S. Z., Liu, H., Chen, J., Orpe, A., Zhao, D., & Lu, G. Q. (2011). Extension of the Stöber method to the preparation of monodisperse resorcinol–formaldehyde resin polymer and carbon spheres. Angewandte Chemie International Edition, 50(26), 5947-5951.
- Liu, M., Zhang, Y., Sun, S., Khan, A. R., Ji, J., Yang, M., & Zhai, G. (2019). Recent advances in electrospun for drug delivery purpose. Journal of drug targeting, 27(3), 270-282.
- Livage, J., Henry, M., & Sanchez, C. (1988). Sol-gel chemistry of transition metal oxides. Progress in solid state chemistry, 18(4), 259-341.
- Locke, J. E., Sharma, S., and Chan, C. (2007). Construction of a database for the acoustical characteristics of fibers and foams used for aircraft interior noise treatment. Nationwide Inpatient Sample (NIS) Rep. to National Institute for Aviation Research (NIAR), Wichita State Univ., Wichita, KS.
- Loría-Bastarrachea, M. I., Herrera-Kao, W., Cauich-Rodríguez, J. V., Cervantes-Uc, J. M., Vázquez-Torres, H., & Ávila-Ortega, A. (2011). A TG/FTIR study on the thermal degradation of poly (vinyl pyrrolidone). Journal of thermal analysis and calorimetry, 104(2), 737-742.
- Mahashabde, A. et al. (2011). Assessing the environmental impacts of aircraft noise and emissions. Prog. Aerosp. Sci. 47, 15–52.
- Manville, J. OEM Insulations Division. www.jm.com Available online: https://www.tricityinsulation.com/cms/wp-content/uploads/2010/11/Microlite-Blankets1.pdf (accessed on 2 June 2019).
- Masse, S., Laurent, G., & Coradin, T. (2009). Influence of cyclic polyamines on silica formation during the Stöber process. Physical Chemistry Chemical Physics, 11(43), 10204-10210.
- Masse, S., Laurent, G., Chuburu, F., Cadiou, C., Déchamps, I., & Coradin, T. (2008). Modification of the Stöber process by a polyazamacrocycle leading to unusual core- shell silica nanoparticles. Langmuir, 24(8), 4026-4031.
- Mettler-Toledo International Inc. All Rights Simple Determination of the Thermal Conductivity of Polymers by DSC. Application published in METTLER TOLEDO Thermal Analysis UserCom 22

https://www.mt.com/es/es/home/supportive\_content/matchar\_apps/MatChar\_UC226.html

- Mit-uppatham, C., Nithitanakul, M., & Supaphol, P. (2004). Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter. Macromolecular Chemistry and Physics, 205(17), 2327-2338.
- Møller, M. F. (1993). A scaled conjugate gradient algorithm for fast supervised learning. Neural networks, 6(4), 525-533.
- Na, H., Chen, P., Wan, K. T., Wong, S. C., Li, Q., Ma, Z. (2012). Measurement of adhesion work of electrospun polymer membrane by shaft-loaded blister test. Langmuir, 28, 6677-6683.
- Najem, J. F., Wong, S. C., Ji, G. (2014). Shear adhesion strength of aligned electrospun nanofibers. Langmuir, 30, 10410-10418.
- Nakajima, K., Noma, R., Kitano, M., & Hara, M. (2013). Titania as an early transition metal oxide with a high density of Lewis acid sites workable in water. The Journal of Physical Chemistry C, 117(31), 16028-16033.
- Nakata, K., & Fujishima, A. (2012). TiO2 photocatalysis: Design and applications. Journal of photochemistry and photobiology C: Photochemistry Reviews, 13(3), 169-189.
- Nasouri, K., Shoushtari, A. M., & Mojtahedi, M. R. M. (2015). Effects of polymer/solvent systems on electrospun polyvinylpyrrolidone nanofiber morphology and diameter. Polymer Science Series A, 57(6), 747-755.
- Newsome, T. E., & Olesik, S. V. (2014). Electrospinning silica/polyvinylpyrrolidone composite nanofibers. Journal of Applied Polymer Science, 131(21).
- Nixon, A., Burchell, M. J., Price, M. C., Kearsley, A. T., & Jones, S. (2012). Aerogel tracks made by impacts of glycine: Implications for formation of bulbous tracks in aerogel and the Stardust mission. Meteoritics & Planetary Science, 47(4), 623-633.
- Ohtani, B., Ogawa, Y., & Nishimoto, S. I. (1997). Photocatalytic activity of amorphous– anatase mixture of titanium (IV) oxide particles suspended in aqueous solutions. The Journal of Physical Chemistry B, 101(19), 3746-3752.
- Pant, H. R., Pant, B., Pokharel, P., Kim, H. J., Tijing, L. D., Park, C. H., ... & Kim, C. S. (2013). Photocatalytic TiO2–RGO/nylon-6 spider-wave-like nano-nets via electrospinning and hydrothermal treatment. Journal of membrane science, 429, 225-234.
- Parida, D., Moreau, E., Nazir, R., Salmeia, K. A., Frison, R., Zhao, R., ... & Gaan, S. (2021). Smart hydrogel-microsphere embedded silver nanoparticle catalyst with high activity and selectivity for the reduction of 4-nitrophenol and azo dyes. Journal of Hazardous Materials, 126237.
- Park, H., Park, Y., Kim, W., & Choi, W. (2013). Surface modification of TiO2 photocatalyst for environmental applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 15, 1-20.
- Park, S. J., & Jin, F. L. (2004). Thermal stabilities and dynamic mechanical properties of sulfonecontaining epoxy resin cured with anhydride. Polymer degradation and stability, 86(3), 515-520.
- Park, S. J., Jang, Y. S., & Rhee, K. Y. (2002). Interlaminar and ductile characteristics of carbon fibers-reinforced plastics produced by nanoscaled electroless nickel plating on carbon fiber surfaces. Journal of colloid and interface science, 245(2), 383-390.

- Park, Y. J., Joo, H. S., Kim, H. J., Lee, Y. K. (2006). Adhesion and rheological of EVA-based hot-melt adhesives. International Journal of Adhesion & Adhesives, 26, 571-576
- Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., ... & Dionysiou, D. D. (2012). A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental, 125, 331-349.
- Peniche, C., Zaldívar, D., Pazos, M., Páz, S., Bulay, A., & Román, J. S. (1993). Study of the thermal degradation of poly (N-vinyl-2-pyrrolidone) by thermogravimetry–FTIR. Journal of applied polymer science, 50(3), 485-493.
- Periyat, P., Baiju, K.V., Mukundan, P., Pillai, P.K., Warrier, K.G.K. (2007). Aqueous colloidal sol– gel route to synthesize nanosized ceria-doped titania having high surface area and increased anatase phase stability. J. Sol-Gel Sci. Technol. 43(3), 299–304.
- Periyat, P., Saeed, P.A., Ullattil, S.G. (2015). Anatase titania nanorods by pseudo-inorganic templating. Mater. Sci. Semicond. Process. 31, 658–665.
- Pielichowski, K., Njuguna, J., Janowski, B., & Pielichowski, J. (2006). Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. In Supramolecular Polymers Polymeric Betains Oligomers (pp. 225-296). Springer, Berlin, Heidelberg.
- Pirozzi, D., Imparato, C., D'Errico, G., Vitiello, G., Aronne, A., & Sannino, F. (2020). Threeyear lifetime and regeneration of superoxide radicals on the surface of hybrid TiO2 materials exposed to air. Journal of hazardous materials, 387, 121716.
- Pope, E. J. A., & Mackenzie, J. D. (1986). J. of Non-Cryst. Solids, 87, 185.
- Prokop, A., Iwasaki, Y., & Harada, A. (2014). Intracellular Delivery II.
- Prouzet, É., & Boissière, C. (2005). A review on the synthesis, structure and applications in separation processes of mesoporous MSU-X silica obtained with the two-step process. Comptes Rendus Chimie, 8(3-4), 579-596.
- Qiu, B., Xing, M., & Zhang, J. (2015). Stöber-like method to synthesize ultralight, porous, stretchable Fe 2 O 3/graphene aerogels for excellent performance in photo-Fenton reaction and electrochemical capacitors. Journal of Materials Chemistry A, 3(24), 12820-12827.
- Ramakrishna, S. (2005). An introduction to electrospinning and nanofibers. World scientific.
- Ramirez, A., Lopez, B. L., & Sierra, L. (2003). Study of the acidic sites and their modifications in mesoporous silica synthesized in acidic medium under quiescent conditions. The Journal of Physical Chemistry B, 107(35), 9275-9280.
- Reich, E., Schibli, A. (2007). High-Performance Thin-Layer Chromatography for the Analysis of Medicinal Plants; Thieme Medical Publishers: New York, NY, Chapter 2, p 22.
- Reppe, W., Curt, S., Adolf, H. (1941). Polymeric N-vinyl lactams and process of producing same. US patent 2265450.
- Reppe, W., Kraikallz, H., Dornbelm, O., Sauerbier, R. (1943). N-vinyl lactams. US patent 2317804.
- Rhim, J. W. (2004). Physical and mechanical properties of water-resistant sodium alginate films. LWT-Food science and technology, 37(3), 323-330.

- Rieger, K. A., Birch, N. P., & Schiffman, J. D. (2013). Designing electrospun nanofiber mats to promote wound healing–a review. Journal of Materials Chemistry B, 1(36), 4531-4541.
- Ripley, B. D. (2002). Modern applied statistics with S. Springer.
- Ripley, B. D. (2007). Pattern recognition and neural networks. Cambridge university press.
- Rogina, A. (2014). Electrospinning process: Versatile preparation method for biodegradable and natural polymers and biocomposite systems applied in tissue engineering and drug delivery. Applied Surface Science, 296, 221-230.
- Roh, S. H., Lee, Y. A., Lee, J. W., & Kim, S. I. (2008). Preparation and characterization of electrospun silica nanofibers from PVP/P123 blended polymer solution. Journal of nanoscience and nanotechnology, 8(10), 5147-5151.
- Rutledge, G. C., Fridrikh, S. V. (2007). Formation of fibers by electrospinning. Adv. Drug Deliv. Rev. 59, 1384–1391;
- Saleh, T. A., Al-Ruwayshid, S. H., Sarı, A., & Tuzen, M. (2020). Synthesis of silica nanoparticles grafted with copolymer of acrylic acrylamide for ultra-removal of methylene blue from aquatic solutions. European Polymer Journal, 130, 109698.
- Sanchez, C., Belleville, P., Popall, M., & Nicole, L. (2011). Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market. Chemical Society Reviews, 40(2), 696-753.
- Sanchez, C., Julián, B., Belleville, P., & Popall, M. (2005). Applications of hybrid organic– inorganic nanocomposites. Journal of Materials Chemistry, 15(35-36), 3559-3592.Kickelbick, G. (2007). Introduction to hybrid materials. Hybrid materials, 1, 2
- Sannino, F., Pernice, P., Imparato, C., Aronne, A., D'Errico, G., Minieri, L., ... & Pirozzi, D. (2015). Hybrid TiO 2–acetylacetonate amorphous gel-derived material with stably adsorbed superoxide radical active in oxidative degradation of organic pollutants. RSC advances, 5(114), 93831-93839.
- Sawicka, K. M., & Gouma, P. (2006). Electrospun composite nanofibers for functional applications. Journal of Nanoparticle Research, 8(6), 769-781.
- Scanlon, D., Dunnill, C., Buckeridge, J. et al. (20013). Band alignment of rutile and anatase TiO2. Nature Mater 12, 798–801.
- Schlipf, D. M., Jones, C. A., Armbruster, M. E., Rushing, E. S., Wooten, K. C., Rankin, S. E., & Knutson, B. L. (2015). Flavonoid adsorption and stability on titania-functionalized silica nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 478, 15-21.
- Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., & Bahnemann, D. W. (2014). Understanding TiO2 photocatalysis: mechanisms and materials. Chemical reviews, 114(19), 9919-9986.
- Schubert, U. (2003). Silica-based and transition metal-based inorganic-organic hybrid materials—A comparison. Journal of sol-gel science and technology, 26(1-3), 47-55.
- Schubert, U. (2005). Chemical modification of titanium alkoxides for sol-gel processing. J. Mater. Chem. 15(35–36), 3701–3715.

- Sell, S. A., Wolfe, P. S., Garg, K., McCool, J. M., Rodriguez, I. A., & Bowlin, G. L. (2010). The use of natural polymers in tissue engineering: a focus on electrospun extracellular matrix analogues. Polymers, 2(4), 522-553.
- Seo, J., Lee, H., Lee, H. J., Kim, M. S., Hong, S. W., Lee, J., ... & Lee, C. (2018). Visible light-photosensitized oxidation of organic pollutants using amorphous peroxo-titania. Applied Catalysis B: Environmental, 225, 487-495.
- Sethi, S., Ge, G., CI, L., Ajayan, P. M., Dhinojwala, A. Gecko-inspired carbon nanotube-based self-cleaning adhesives. Nano Letters, 8 (2008), 822-825.
- Shan, A. Y., Ghazi, T. I. M., & Rashid, S. A. (2010). Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: a review. Applied Catalysis A: General, 389(1-2), 1-8.
- Shao, C., Kim, H., Gong, J., & Lee, D. (2002). A novel method for making silica nanofibres by using electrospun fibres of polyvinylalcohol/silica composite as precursor. Nanotechnology, 13(5), 635.
- Sharma, N., McKeown, S. J., Ma, X., Pochan, D. J., & Cloutier, S. G. (2010). Structure- property correlations in hybrid polymer- nanoparticle electrospun fibers and plasmonic control over their dichroic behavior. ACS nano, 4(10), 5551-
- Sill, T. J., & Von Recum, H. A. (2008). Electrospinning: applications in drug delivery and tissue engineering. Biomaterials, 29(13), 1989-2006.
- Singh, S., Mahalingam, H., & Singh, P. K. (2013). Polymer-supported titanium dioxide photocatalysts for environmental remediation: A review. Applied Catalysis A: General, 462, 178-195.
- Stani, M. M., Muellner, H., Plotizin, I., & Zlabinger, K. (2005, July). Sound insulation of plasterboard walls and airflow resistivity: an empirical examination with respect to practical applications. In Proc. Forum Acusticum (pp. 1987-1992).
- Stöber, W., Fink, A., & Bohn, E. (1968). Controlled growth of monodisperse silica spheres in the micron size range. Journal of colloid and interface science, 26(1), 62-69.
- Sun, B., Duan, B., Yuan, X. (2006). Preparation of core/shell PVP/PLA ultrafine fibers by coaxial electrospinning. Journal of Applied Polymer Science, 102, 30-45.
- Tarnow, V. (2002). Measured anisotropic air flow resistivity and sound attenuation of glass wool. The Journal of the Acoustical Society of America, 111(6), 2735-2739.
- Taylor, G. I. (1969). Electrically driven jets. Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 313(1515), 453-475.
- Teo, W. E., Ramakrishna, S. (2006). A review on electrospinning design and nanofibre assemblies. Nanotechnology. 17, 89–106.
- Tobing, S. D., Klein, A. (2001). Molecular parameters and their relation to the adhesive performance of acrylic pressure-sensitive adhesives. Journal of Applied Polymer Science, 79, 2230-2244.
- Toki, M., Chow, T. Y., Ohnaka, T., Samura, H., & Saegusa, T. (1992). Structure of poly (vinylpyrrolidone)-silica hybrid. Polymer Bulletin, 29(6), 653-660.

- Trematerra, A., Iannace, G., Nesti, S., Fatarella, E., & Peruzzi, F. (2014, September). Acoustic properties of nanofibers. In Proceedings of Forum Acusticum. 7th Forum Acusticum, FA 2014.
- Van Blaaderen, A., Van Geest, J., & Vrij, A. (1992). Monodisperse colloidal silica spheres from tetraalkoxysilanes: particle formation and growth mechanism. Journal of colloid and interface science, 154(2), 481-501.
- Van Helden, A. K., Jansen, J. W., & Vrij, A. (1981). Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents. Journal of Colloid and Interface Science, 81(2), 354-368.
- Varma, H.K., Mani, T.V., Damodaran, A.D., Warrier, K.G., Balachandran, U. (1994). Characteristics of alumina powders prepared by spray-drying of boehmite sol. J. Am. Ceram. Soc. 77(6), 1597–1600.
- Vives, S., & Meunier, C. (2008). Influence of the synthesis route on sol-gel SiO2–TiO2 (1: 1) xerogels and powders. Ceramics International, 34(1), 37-44.
- Wachtler, M., Ostrovskii, D., Jacobsson, P., & Scrosati, B. (2004). A study on PVdF-based SiO2-containing composite gel-type polymer electrolytes for lithium batteries. Electrochimica Acta, 50(2-3), 357-361.
- Wang, L., Zhang, L., & Tian, M. (2012). Improved polyvinylpyrrolidone (PVP)/graphite nanocomposites by solution compounding and spray drying. Polymers for Advanced Technologies, 23(3), 652-659.
- Wang, N., Wang, X., Jia, Y., Li, X., Yu, J., & Ding, B. (2014a). Electrospun nanofibrous chitosan membranes modified with polyethyleneimine for formaldehyde detection. Carbohydrate polymers, 108, 192-199.
- Wang, T., Lei, C. H., Dalton, A. B., Creton, C., Lin, Y., Fernando, K. A. S., Sun, Y. P., Manea, M., Asua, J. M., Keddie, J. L. (2006). Waterborne, nanocomposite pressure-sensitive adhesive adhesives with high tack energy, optical transparency, and electrical conductivity. Advanced Materials, 18, 2730-2734.
- Wang, X., Li, Y., Li, X., Yu, J., Al-Deyab, S. S., & Ding, B. (2014b). Equipment-free chromatic determination of formaldehyde by utilizing pararosaniline-functionalized cellulose nanofibrous membranes. Sensors and Actuators B: Chemical, 203, 333-339.
- Wen, S., Liu, L., Zhang, L., Chen, Q., Zhang, L., & Fong, H. (2010). Hierarchical electrospun SiO2 nanofibers containing SiO2 nanoparticles with controllable surface-roughness and/or porosity. Materials Letters, 64(13), 1517-1520.
- Westre, W. N., & Evans, D. W. (2007). U.S. Patent No. 7,182,291. Washington, DC: U.S. Patent and Trademark Office.
- Xiang, H. F., Tan, S. X., Yu, X. L., Long, Y. H., Zhang, X. L., Zhao, N., & Xu, J. (2011). Sound absorption behavior of electrospun polyacrylonitrile nanofibrous membranes. Chinese Journal of Polymer Science, 29(6), 650-657.
- Yang, G. Z., Li, H. P., Yang, J. H., Wan, J., & Yu, D. G. (2017). Influence of working temperature on the formation of electrospun polymer nanofibers. Nanoscale research letters, 12(1), 1-10.

- Yang, Q., Li, Z., Hong, Y., Zhao, Y., Qiu, S., Wang, C., Wei, Y. (2004). Influence of solvents on the formation of ultrathin uniform poly(vinyl pirrolidone) nanofibers with electrospinning. Journal of Polymer Science: Part B: Polymer Physics, 42, 3721-3726.
- Zeng, J., Haoqing, H., Schaper, A., Wendorff, J. H., & Greiner, A. (2003). Poly-L-lactide nanofibers by electrospinning–Influence of solution viscosity and electrical conductivity on fiber diameter and fiber morphology. e-Polymers, 3(1).
- Zhang, Y., Chen, Y., Westerhoff, P., Hristovski, K., & Crittenden, J. C. (2008). Stability of commercial metal oxide nanoparticles in water. Water research, 42(8-9), 2204-2212.
- Zhang, Z., Maggard, P.A. (2007). Investigation of photocatalytically-active hydrated forms of amorphous titania, TiO2·nH2O, Journal of Photochemistry and Photobiology A: Chemistry 186 8–13.
- Zhao, D.; Li, X.Y. (2015). A review of acoustic dampers applied to combustion chambers in aerospace industry. Prog. Aerosp. Sci., 74, 114–130.
- Zheng, M., Gu, M., Jin, Y., & Jin, G. (2000). Preparation, structure and properties of TiO2–PVP hybrid films. Materials Science and Engineering: B, 77(1), 55-59.
- Zywitzki, D., Jing, H., Tüysüz, H., & Chan, C. K. (2017). High surface area, amorphous titania with reactive Ti3+ through a photo-assisted synthesis method for photocatalytic H2 generation. Journal of Materials Chemistry A, 5(22), 10957-10967.

## **Scientific Contributions**

The research activity carried out in the framework of this PhD course contributed to date to six publications on peer-reviewed journals. Four of these deal with the topic of the PhD dissertation:

- "Electrospinning of PVP-based ternary composites containing SiO<sub>2</sub> nanoparticles and hybrid TiO<sub>2</sub> microparticles with adsorbed superoxide radicals" Passaro, J. Imparato, C., Parida, D., Bifulco, A., Branda, F., Aronne, A. *Composites Part B: Engineering* (article being published).
- "Water resistant self-extinguishing low frequency soundproofing polyvinylpyrrolidone based electrospun blankets". Passaro, J., Russo, P., Bifulco, A., ...Marulo, F., Branda, F. *Polymers*, 2019, 11(7), 1205.
- "Artificial neural network-based models for predicting the sound absorption coefficient of electrospun poly(vinyl pyrrolidone)/silica composite". Ciaburro, G., Iannace, G., Passaro, J., ...Marulo, F., Branda, F. *Applied Acoustics*, 2020, 169, 107472.

- "Development of hybrid titanium oxide-based systems for the surface stabilization of reactive oxygen radicals" Imparato, C., Passaro, J., Bifulco, A., Branda, F., Pirozzi, D., Aronne, A. *Chemical Engineering Transactions*, 2021, 84, pp. 139–144.
- "Acoustic improvements of aircraft headrests based on electrospun mats evaluated through boundary element method". Giannella, V., Branda, F., Passaro, J., ...Barbarino, M., Citarella, R. *Applied Sciences* (Switzerland), 2020, 10(16), 5712.
- "Non monotonous effects of noncovalently functionalized graphene addition on the structure and sound absorption properties of Polyvinylpyrrolidone (1300 kDa) electrospun mats". Del Sorbo, G.R., Truda, G., Bifulco, A., Passaro, J., ...Marulo, F., Branda, F. *Materials*, 2018, 12(1), 108.

Three publications pertain other topics in polymer chemistry, chemical engineering and sol-gel science:

- "Structure and Bottom-up Formation Mechanism of Multisheet Silica-Based Nanoparticles Formed in an Epoxy Matrix through an in Situ Process" Branda, F., Bifulco, A., Jehnichen, D., Parida, D., Pauer, R., Passaro, J., Gaan, S., Pospiech, D., Durante, M. *Langmuir* 2021, 37(29), pp. 8886–8893.
- "A new strategy to produce hemp fibers through a waterglass-based ecofriendly process". Bifulco, A., Silvestri, B., Passaro, J., ...Branda, F., Durante, M. *Materials*, 2020, 13(8), 1844.
- "Thermal and fire behavior of a bio-based epoxy/silica hybrid cured with methyl nadic anhydride". Bifulco, A., Marotta, A., Passaro, J., ...Malucelli, G., Branda, F. *Polymers*, 2020, 12(8), 1661.

The personal contributions of the author to the following national and international conferences can be mentioned:

- "Innovative electrospun polyvinylpyrrolidone based materials for soundproofing" Passaro, J., Bifulco, A., Marulo, F., Costantini, A., Branda, F. *Proceedings of 2020 International Congress on Noise Control Engineering*, INTER-NOISE 2020 (oral presentation).
- "Innovative PVP-based composite made by electrospinning". Jessica Passaro, Aurelio Bifulco, Claudio Imparato, Antonio Aronne, Francesco Branda *XXVII*

*CONGRESSO NAZIONALE DELLA SOCIETÀ CHIMICA ITALIANA* – 14-23 Settembre 2021 (poster presentation).

- "Electrospun Polyvinylpyrrolidone for Soundproofing". Jessica Passaro, Aurelio Bifulco, Paolo Russo, Francesco Marulo, Antonio Vecchione, Francesco Branda. Summer School and Workshop in Calorimetry and Thermal Analysis 2019 - Calorimetry and thermal methods in material science, Lione (France) 16-21 June 2019 (poster presentation).
- "Electrospun polyvinylpyrrolidone for soundproofing". Jessica Passaro, Francesco Branda, Joshua Avossa, Aurelio Bifulco, Francesco Marulo, Giuseppe Petrone and Michele Guida. MERCK & ELSEVIER YOUNG CHEMISTS SYMPOSIUM - MEYCS 2018 | RIMINI An international conference for young researchers (chemistry & materials science) Rimini (Italy) 19 – 21 November 2018 (poster presentation).