



Hybrid Sol gel organic-inorganic nanocomposites: Formation, Characterization, and Applications

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Abstract

Recently, one of the biggest challenges for scientific researchers is developing and fabricating engineering nanomaterials with the ability to control the size and morphology for use in multi-applications such as electro-magneto optoelectronic devices, drug delivery, catalysts, fuel cells, sensors, Li-ion batteries, and water treatment. Hybrid organic-inorganic nanocomposites are an interesting class of hybrid materials with interesting applications ranging from encapsulation, sensors, full cells, drug delivery, and controlled release of active substances to their utilization as fillers for the paint and coating industries.

The sol-gel process is considered one of the most practical chemical methods for preparing high purity and chemically homogeneous coatings, membranes, fibers, sheets, ceramics, and powders at low temperatures. Therefore, the sol-gel method was the most practiced technique to the wide area including not only glasses, thin films, and ceramics, but, organic and biomaterials to produce materials of new compositions with high purity, high homogeneity, and to control particle size distributions in a nanoscale level.

The introduction of various organic functional groups, such as amino, glycidol, epoxy, hydroxyl, etc., into alkoxides monomers, leads to sol-gel glasses modified organically. The synthesis of organic-inorganic composites gives a route to produce silicate materials with continuously control chemical and physical properties by simply changing the precursors employed their molar ratio or both. Looking to the future of hybrid composite materials, the new generations of these materials, which are produced from the very fruitful activities in this scientific field, will present promising various applications in different fields: environment, optics, electronics, mechanics, energy, biology, medicine.

Keywords: Sol-gel method; silica; organic-inorganic composites; Hybrid nanocomposites.

1. Introduction

Recent, nanoscience and nanotechnology developments and the desire for new functions generate an enormous demand for very broad and multidisciplinary novel materials. Many types of the well-known materials, such as metals, thin films, ceramics and membranes cannot fulfill all required technological for different new emerging applications [1–5].

The nanoscale materials one enters a world where the fields of physics and chemistry meet and provide a novel properties of engineering materials. In chemistry, the nanoscale range of sizes has been associated with colloids, hydrogels, polymer

molecules, phase-separated regions of the copolymers and similar structures [6–8]. The sol–gel technique is one of the most chemical methods used to prepare the nanostructures and hybrid organic–inorganic materials, based on the hydrolysis and condensation reactions, a versatile process that allows for the production of different engineering materials such as glasses, thin films and ceramics at low temperature [9–12].

The engineering of sol–gel process is appearing as a new branch of development of functional materials with the stable metal sols (the state of matter before gelation), colloids (building blocks with nanosized particles surrounded by a solvent in the matrix) and

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Receive Date: 30 December 2021; Revise Date: 31 January 2022; Accept Date: 08 March 2022.

DOI: [10.21608/EJCHEM.2022.113871.5173](https://doi.org/10.21608/EJCHEM.2022.113871.5173).

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gels with extended three-dimensional structures [13–17].

Besides the progressing in purely inorganic porous solids materials, another innovation for the fabrication and modification of porous nanomaterials appeared at the beginning of the 1990s by the incorporation of organic molecules as constituents of the structure. The sol-gel method offers the potential to synthesize hybrid organic-inorganic composites, combining the distinguished properties of organic and inorganic phases [18–22].

Chemical strategies for formation of organic-inorganic networks, able to direct the assembling of a large variety of structurally well defined nano-scales into the hybrid matrices, which organized in terms of structure and functions. Indeed, the so-called hybrid organic-inorganic composite materials are not facile and simply physical mixtures [23,24].

The hybrids with organic molecules and inorganic components are homogeneous systems derived from monomers and organic molecules and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components' phases in the nano-meters [23,25,26]. Metal-organic frameworks (MOFs), which are consisted of metal ions or clusters and bridging organic molecules, as an important family of porous nano-materials [27–32].

The studies of hybrid nanocomposites as biphasic nanocomposite materials, where the organic molecules and inorganic ions are mixed at nano-sized scale have a considerable interest for using in various applications [23,24,33].

Hybrid organic-inorganic (O/I) nano-materials are defined as colloidal particles that consist of organic molecules and inorganic domains. The properties of hybrid organic-inorganic composite materials are not just the sum of the advantages of both phases' inorganic and organic, but are derived from their synergic effect and creating a new class of engineering hybrid nano-materials [34,35].

The main idea to combine organic parts with the inorganic matrices appears now has evidence, due to the superposition of design associated for formation of materials, it has led the chemists and physicist to imagine numerous of researches more or less easy to applied experimentally [35].

Scientists and engineers worked early on those mixtures of different type materials formed by the

introduction of a macro or nano- structural material into a second substance (the matrix) can show superior properties compared with their pure phases, producing new engineering materials well structural and mechanical properties and a well-known example is inorganic fiber-reinforced polymers [36,37].

Where, the mechanical properties in the hybrid nanocomposite materials are regarded as the most important features of a material are of particular interest. The advancing in the new characterization techniques at the molecular and nanometer scales has been a driving force towards imagination of hybrid nanocomposites in different fields such as optoelectronic, sensors, energy storage, electronics, optics, medicine, catalysis, energy conversion [38,39].

Organic-inorganic hybrid matrices can be utilized in various branches of engineering materials chemistry because they are simplicity to process and are flexible to fabricate on the molecular and nano-scale [6,40].

2. Advances

Nowadays, there are four major topics in the preparation of organic-inorganic hybrid nanocomposite materials:

(a) their molecular engineering, (b) their nano- and micro-meter organization, (c) the transformation from functional to multifunctional hybrids systems, and (d) their combination with natural origin molecules and bioactive components.

The knowledge of the chemical processes occurring at contact of macro- and nanoparticles with a specific solution or polymeric matrix, which depend on the polymeric material and its chemical nature, may help in the designing and production of materials to be used for different industrial applications with the protection of the natural environment [28,41].

In particular the sol-gel route based on silicon was one of the most leading forces what has become the wide and superior field of hybrid organic-inorganic networks obtained through hydrolysis of organically modified metal alkoxides or metal halides polycondensed with or without simple metallic alkoxides. The reason for the special role of silicon was its good processability, the formation of a cross-linked system and with chemical stability of the Si—C bond during the formation of a silica network which allowed the

production of organic-inorganic networks in one chemical step [42,43].

Actually, its unique characteristics, such as low cost, low-temperature processing and shaping, high sample homogeneity and purity, availability of various metallo-organic precursors and the processing ease and versatility of the colloidal phase, allow the fabrication of multifunctional hybrid organic-inorganic structures through a molecular nanotechnology approach based on tailoring assembly of organic and inorganic building blocks [44,45].

Low temperature sol-gel route makes it possible to produce networks involving organic compounds or polymers to lead to hybrid materials for which organic and inorganic phases coexist, with high purity and high homogeneity. Furthermore, the sol-gel process can be used to make multi-component matrices which cannot be made by conventional methods due to crystallization [46,47].

Thus, preparation of different nanoscale structures, particles and composites has gained the interest and focusing for developing new engineering nanomaterials and devices. Currently, the nanogel, clusters, nanoparticles, nanorods, nanowires, nanotubes and polynucleotides, and functional supramolecular nanostructures are considered as potential building blocks for nanotechnology, nanoelectronic and nanomagnetic devices and circuits.

3. Sol-gel process

Nanoparticles materials and their nanotechnology can display properties that differ from their bulk counterpart. Sol-gel process has become a flexible route for synthesizing nanoparticles, nanoceramics, thin films and organic inorganic nanocomposites, since its key difficulty of crack failure has been overcome by two approaches: the use of iterative spin coating and flash annealing to yields oxidic networks based on $-\text{[Si-O]}_n-$ or $-\text{[M-O]}_n-$ [48–50].

This process is chemically based on organic polycondensation processes in which small molecules form polymeric structures and this reaction results in a three-dimensional (3-D) cross-linked network. The sol-gel technique uses different types of metal alkoxides, which undergo the hydrolysis and polycondensation polymerization reactions to form gels materials [51,52].

The basic reactions (hydrolyses and condensation) which occur during the formation of the inorganic

network followed by the reactivity of the precursors to nucleophilic reactions are considered. The fact that small molecules are used as starting components for the synthesis of the crosslinked materials reveals various advantages, for example a high control of the purity and composition (ease of producing and introducing a wide variety of dopants) of the final produced materials and the use of a solvent-based chemistry which offers several advantages for the chemical processing of the results materials. During the sol-gel synthesis, the viscosity for the formed solution gradually increases as the sol (colloidal suspension of small particles, 1nm -100 nm) become chemically interconnected through polycondensation reactions to form a rigid, porous network (gel) [53,54].

The interest in sol-gel materials and technology is not only related to their physical and chemical properties, but also to the possibilities of very different material processing in desired shapes at low temperature used in different applications [55,56].

Fig.1 represents a flow chart of different sol gel processing routes for preparing different materials such as powders, fibers, films, gels, aerogels, xerogels, or dense ceramics from the same sol.

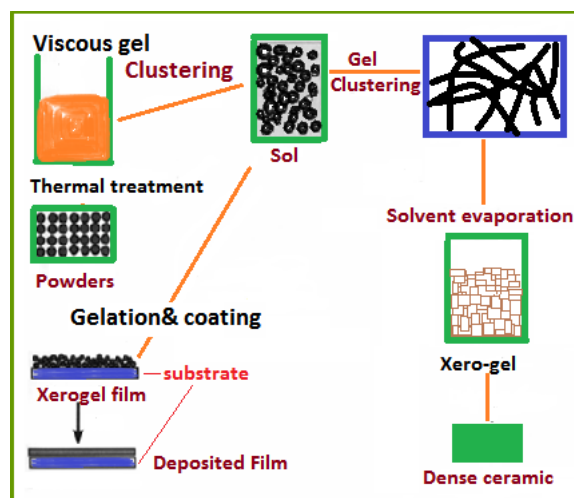


Fig.1 Overview of flow chart for the different sol-gel routes.

The formation of pure silica gel via hydrolysis of tetraethylorthosilicate, $[\text{TEOS}, \text{Si}(\text{OC}_2\text{H}_5)_4]$ in acidic medium for the productions of glass-like structures in various forms such as fibers, powder, optical lenses and composite glass [57,58].

The most difficulty in preparation of conventional ceramics is the need of high temperature during

processing and the difficulty in producing the complex geometrical configurations materials. Roy et al.[59] using sol gel process for preparation a different types of ceramic oxide compositions using Al, Si, Ti, Zn, etc., with high chemical homogeneity, which could not be produced by traditional ceramic technology [60].

The sol gel process also makes possible preparation of materials that are hard to produce by conventional methods because of some problems associated with the synthesis processes as high melting temperatures, volatilization or crystallization. Different factors may influence in the sol-gel process such as: H₂O/Si molar ratio, nature of the solvent, pH, type of catalyst, temperature, chemical additives. Finally, the sol-gel approach is adaptable to producing glasses and fibers as well as bulk pieces as in the Fig.2.

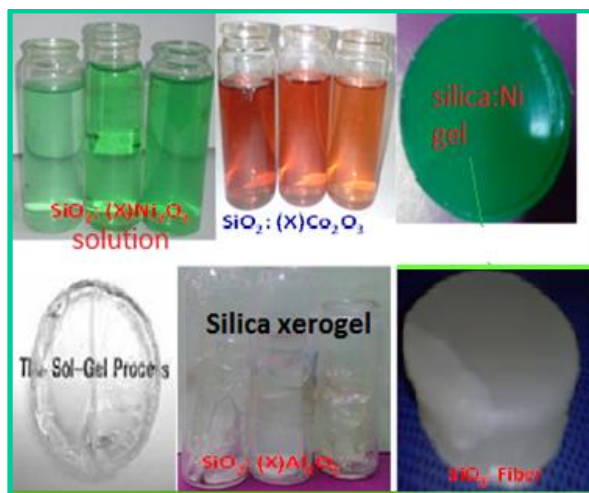


Fig.2 Reaction scheme of sol-gel process form sol-gel -xeogel.

3.1. Chemistry of sol-gel process for Metal alkoxides silicates and non-silicates

The sol-gel technique comprises solution, gelation, drying, and densification. The preparation of a sol-gel silica glass begins with an alkoxide monomers (such as tetramethyl and tetraethyl orthosilicate) (TMOS or TEOS) which is mixed with water and a mutual organic solvent to form a solution during the hydrolysis [61,62].

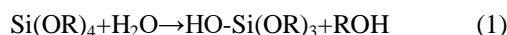
Where, ethyl groups are the most known alkoxy groups, methoxy, butoxy, propoxy and other long-chain alkoxy groups are also used in alkoxy silanes. Metal alkoxides or (organometallic compounds) are

used in sol-gel methods starting materials with metal alkoxides such as TEOS or alkoxy borates [63].

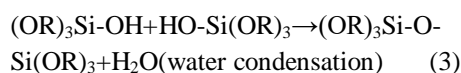
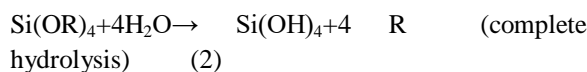
The basic structure or morphology of the produced solid phase can range from discrete colloidal particles to a continuous chain-like polymeric network [64,65].

Hydrolysis resulted in the formation of silanol groups (Si—OH). These species are only intermediates, which react to link together to form siloxanes. Subsequent condensation reactions produce siloxane bonds (Si—O—Si) in short-range order, finally through poly- condensation silanols react with siloxanes to produce xero-gels after aging and drying processes under ambient atmospheres forming porous matrices [9,66,67].

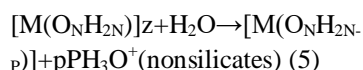
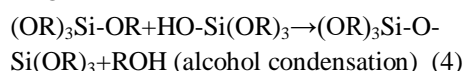
The sol-gel transition from sol to gel at the functional group level can be described by three reactions: hydrolysis, condensation and polycondensation (Equations 1-3) and equation (5) for nonsilicates [68]].



Where, (R) represents a proton or other ligand, OR is an alkoxy group and ROH alcohol.



Or



Non-silicate metal alkoxides are very reactive with water; where the hydrolysis rate of titanium alkoxide is generally up to 10⁵ times faster than for the corresponding silicon alkoxide. This type of polycondensation reaction can continue to build large silicon containing molecules during the polymerization process forming a polymer, which is defines a huge molecule called macromolecule [9,69].

These colloidal gels are perfectly appropriate for the synthesis of multi-component glasses, thin films and ceramics. By comparing the transition metal

alkoxides show a lower electronegativity with silicon which causes them to be more electrophilic and less stable towards hydrolysis in the sol–gel reactions.

4. Fundamental reactions in the sol–gel process based on tetraalkoxysilanes (TEOS).

The silica-based sol–gel method is considered the most one that has been investigated; hence, the basic principles of reaction are usually discussed using this process as a model system. The important fact that makes the silica-based sol–gel process a predominant process in the preparation of hybrid materials, which is the simple incorporation of organic groups using organically modified silanes [70].

Usually, the Si–C bonds enhanced stability against hydrolysis in the aqueous media, which is not the case for many metal–carbon bonds, so it is possible to easily incorporate a large variety of organic groups in the end product [71].

Chemically, $R_{4-n}SiX_n$ compounds are used as starting molecular precursors, in which the Si–X bond is labile towards hydrolysis reactions producing Si–OH unstable silanols that condensate forming (Si–O–Si) bonds. From the catalysis of the monomeric starting precursor, reactive alkoxide monomers (the hydrolyzed alkoxide), dimers, trimers, oligomers, linear and both polymers and cyclic species (silica rings and cages) can be produced in the order, as can see in Fig. 4. In the first steps of this reaction Dimer, oligo- and polymers as well as cyclics are formed subsequently resulting in colloids that define the sol. The formed rings become a kind of nucleation centre with connected ion and via the addition of monomers and other species three dimensional particles (3DPs) can finally form [2,72].

In aqueous silicates, the oxidation state ($z=4$) is the interesting one in the chemistry of silicon, where the silicon is less electropositive, e.g. the positive charge on silicon $\delta(Si)$ in $Si(OR)_4$ is +0.32, where $\delta(Ti)$ in $Ti(OR)_4$ is 0.63 and $\delta(Zr)$ is +0.65 in $Zr(OR)_4$ [73–75].

The silica gel formed by this process leads to a rigid, interconnected 3D-dimensional network consisting of submicrometer pores and polymeric chains. During the drying process at atmospheric condition, the excess of solvent and liquid are removed and essential shrinkage occurs in the prepared matrix formed the xerogel material [76].

Thermal treatment process of a xerogel at high temperature produces viscous gels and transforms the

porous gel to a dense glass. So, the definition of sol is the dispersion of colloidal particles with diameters ranging from 1nm to 100 nm in a liquid phase. A gel is rigid network with pores dimensions and polymeric chains and the drying process substantially reduces their pores size. The term “gel” is considered combinations of materials that can be classified into four categories:

- (a) Well-ordered lamellar structures,
- (b) Covalent polymeric networks, with disordered,
- (c) Polymeric networks structures with physical aggregation and disordered,
- (d) Particular disordered structures [77].

Films and coatings were the first commercial applications of the sol-gel process. The successful applications sol-gel-based materials include monoliths (lenses, prisms, lasers), fibers (waveguides), controlled porosity, catalyst supports and porous membranes. The pH value of the chemical environment highly affects the outcome products. Low pH values produce fast hydrolysis rate and slow condensation, forming three-dimensional gel. While, the high pH values produce slow hydrolysis and fast poly-condensation, resulting in a suspension of particles, with a mono disperse particles distribution in the chemical phase [78,79].

To investigate homogeneous oxides with predetermined compositions, the difference in reactivity has been minimized by controlled prehydrolysis of the less reactive precursors as $TiCl_4$ and $ZrCl_4$ [26,80].

As example, effect of different parameters such as the pH of the gel, concentration of reactants, gel density, gel ageing on the growth of the Lanthanum tartrate crystals was studied. Where, lanthanum tartrate shows poor solubility in water hence the control on the chemical reaction during the gel method (Fig. 3). The diffusion of Vanadium ions through the narrow pores of the silica-based lead to chemical reaction between these ions and the $C_4H_4O_6^{2-}$ ions. After about 24 h the prepared samples transformed to the gel in summer (32–40°C) and 3–4 days for the gel to set in winter (20–25°C).



Fig. 3 Optical photograph showing growth of Vanadium crystals in different zones of gel at different conditions.

5. Synthesis of sol gel monolithic materials

The drying stage is considered the critical one during formation of monolithic materials. Drying process by slow and simple evaporation rates results in xerogels. When liquid evaporates from the porous gels, the pore walls are subjected to a stress equal to the capillary pressure due to elimination of excess solvents. The capillary pressure for the prepared sol gel materials depends on the properties of the material, OH ratios and the solvent, and is expressed with the Young-Laplace equation [81,82].

$$P_c = 2\gamma_{LV}\cos\theta/r$$

where P is the capillary pressure, γ_{LV} is the liquid-vapor interfacial tension (surface tension), θ is the contact angle and r are the pore radius.

The capillary pressure can be controlled in two ways: 1) decrease of the surface tension between liquid and vapor, 2) increase of the pore radius. Consequently, a common method used to overcome cracking or fraction of monolithic structures is to reduce the capillary pressure as possible by exchange with or addition of a liquid with low surface tension (e.g. alcohols or DMF) [83].

Immersion of porous materials (gels) in glycerol, polyethyleneglycole (PEG) after gelation have also been used to reduce cracking during standard drying and freeze drying [84].

In gels, the first stage of drying, where the liquid-vapor interface remains at the exterior surface, continues while the body shrinks to as little as one-tenth of its original volume. In supercritical drying in the same approach the water is replaced by organic solvent or supercritical CO_2 , make it easy to remove without collapsing the solid matrix [62].

Introduction of other solvents and macroporosity can also be used to retain the monolithic structure during drying [26,62].

During calcinations process, all different organic molecules are removed from the inorganic network by thermal treatment. Calcinations process often produces more mechanically stable materials and the sintering can increase the density of the materials to increase the pore volume and decrease surface area [5,85].

6. Hybrid organic-inorganic nanocomposite materials

During the last two decades the field of hybrid organic-inorganic materials has been growing intensively and is nowadays one of the major fields of research and the most exciting [86,87].

Hybrid organic-inorganic materials will play a main role in the continuous development of functional nanomaterials, which is supported by the growing interest of chemistry, physics, biological and materials scientists, for creating smart engineering materials that benefit from the best of the three realms: organic, inorganic and biological [88].

In practice, the term hybrid is used to denote (biological) inbreed, cars, laptops and (of course in the Netherlands) bikes. Also, within physics and chemistry "hybrid" is used in various contexts. The development of hybrid organic-inorganic materials, which is currently excellent and booming, aims at combining the physical and chemical properties of inorganic particles and organic components, for various applications such as scratch resistance coatings, catalysis, contact lenses, dental filling, drug delivery, sensors, membranes, chromatography, ion extraction, etc. The binding in the hybrid sol gel materials of organic moieties within inorganic matrices mainly depends on the use of silicon-based precursors, owing to the hydrolytic stability of Si-C bond. Organo-functional silanes are the most one used in sol-gel processing, either as a single precursor, or copolymerized with another alkoxide precursor (usually tetraethoxysilane, TEOS). Materials named "ormosils" (organically modified silicas) or "ormocers" (organically modified ceramics) are prepared in this manner. Organosilanes or organophosphorus are also used as coupling agents, to modify the surface of particulate fillers (polymers) or fibers in the field of composite materials, to make molecular catalysts heterogeneous, or to pre pare self-assembled monolayers on silica surfaces.

Recently there are four main topics in the synthesis of organic-inorganic materials: (a) their molecular engineering, (b) their nano- and micrometer-sized organization, (c) the transition from functional to multifunctional hybrids, and finally, (d) the combination with bioactive various components. Recently, many of the colloidal matrices were prepared by chemical methods already known, that reinvestigated by more advanced instrumental

techniques to get new insights into the origin of the specific chemistry and physics behind these materials.

7. Definition and classification: Hybrid materials and nanocomposites

Usually, the term of hybrid material is used for many systems of different materials, such as amorphous systems, highly ordered coordination crystalline polymers, materials with and without chemical interactions between the inorganic and organic building units. Before the discussion of the formation and properties of hybrid composite materials we try to taking into account various concepts of composition and structure (table 1).

Table 1. Different possibilities of composition and network structure of hybrid materials.

materials	type
Matrix	crystalline ↔ amorphous organic ↔ inorganic
Building blocks	molecules ↔ macromolecules ↔ particles ↔ fibres
Interactions between components	strong ↔ weak

The definition of hybrid organic-inorganic material is a composite material that includes two moieties mixed on the nanometer or molecular scale or nanocomposites with organic (or bio) and inorganic components. Generally, one of these compounds is inorganic and the other one organic in nature. The hybrid materials can be classified into two classes (I, II).

In class I the hybrid composite nano-materials are those that show weak chemical interactions between the two phases, such as hydrogen bonding, van der Waals or ionic bonds give cohesion to the whole structure [89,90].

In class II hybrid materials are those that show strong interactions between the components, where the two organic and inorganic phases are totally or partly linked through strong chemical covalent or ionic-covalent bonds, because of the slow change in the chemical interactions with nearly fixed transition between weak and strong interactions. The existence of chemical covalent linkages between organic

molecules and mineral components present numerous advantages: -

- (a) The potential to prepare totally new engineering materials from functionalized alkoxides;
- (b) Minimization of phase separation;
- (c) Better definition of the organic-inorganic interface. Many hybrid materials show both types of chemical interactions and have the ability to be classified either as Class I or Class II hybrids.

In addition to the changes chemical bonding structural properties can also be used to characterize between various classes of hybrid composite materials. If there are no strong chemical interactions between the inorganic and organic blocks, blends are formed as a material is the combination of inorganic clusters with organic polymeric chains with low interaction between the components. If an inorganic particle and an organic blocks mix together without strong chemical interactions, so called interpenetrating networks (IPNs) are formed as in the sol-gel material formed in the presence of a polymeric network or vice versa. The clusters, are covalently bonded to the organic polymeric matrices (Scheme 8 c) or inorganic and organic polymers are covalently connected with each other.

8. Hybrid organic-inorganic nanocomposites.

Nanocomposites materials are functional hybrid materials between the interface of organic and inorganic realms. Therefore, there is a regular transition between hybrid and nanocomposites materials, because large molecular building blocks for hybrid materials, such as large inorganic clusters, can already be of the nanometer length scale. Examples of used inorganic units for nanocomposites are nanoparticles, and nanorods. The nanocomposite is usually formed from these building blocks by their introduction in organic polymeric matrices [91].

Sikong et al.[92] explore a method to improve hydrophilicity of organic compounds (is a molecule attracted to water molecules and dissolved in water) of the surface of farmers that could be more easily dipped produced high quality dipped rubber products by Ni/B/TiO₂nano-composite film. The addition of Ni/B/TiO₂ coating film improve the hydrophilicity, leading to the enhancement of smoothness, increasing rubber film thickness and stable tensile strength of rubber latex film [93].

9. Synthetic Strategies towards Hybrid organic-inorganic Materials

There are two various approaches can be used for the synthesis of hybrid organic-inorganic materials. Either well-defined preformed building blocks are applied that react to form the final hybrid material in which the precursors still nearly keep their original source or one or both structural units are formed from the starting materials that are transformed into a network structure.

Both two approaches have their advantages and disadvantages and will be described here in more detail.

9.1. Building block method:

As mentioned above building blocks at least partially content their molecular integrity in material formation, meaning that structural units that are present in these sources for materials formation can also be found in the final material. Building blocks are consist of a well-defined molecular or nano-structures and of a well-defined size and shape, with a tailored surface structure and composition. The properties of these continuously present in building blocks the matrix formation, which is not the case if material precursors are transferred into network structural materials. As examples of such well-defined building blocks are modified the inorganic particles connected with reactive organic matrix. Cluster materials usually consist of at least one functional group that allows an interaction with an organic system, interacting by copolymerization. According to the number of functional groups that can interact, the building blocks are able to modify an organic system or form partially or fully crosslinked organic-inorganic materials. For example, two reactive functional groups can form a chain structure and three reactive functional groups in the building blocks can be used for the formation of a crosslinked network structure. The nanoscale building blocks, such as nanoparticles or nanorods, can also be used to form nanocomposites. The building block approach for the formation of inorganic or organic materials has one main advantage compared with the in-situ formation: because at least one structural unit is well-defined and without important structural changes during the matrix formation and best performance in the materials' formation. Building blocks can be classified to inorganic or organic in nature, but because they are incorporated into another phase,

they should be somehow compatible with the second phase.

9.1.1. Inorganic building blocks:

The clusters are defined as agglomerates of elements that contain metals or metals in blend with other different elements. The classical chemical meaning of a cluster includes the existence of metal-metal bonds, the term cluster is meaning of an agglomerate of atoms in a given shape. Regularly metal clusters need a surface functionalization with groups that will decrease the surface energy and thus avoid coalescence to larger particles. The aim in the chemical processes of these systems is the formation of clusters carrying organic functionalizations that tailor the interface to an organic matrix by making the inorganic core compatible and the addition of surface functional groups for certain interactions within the matrix. One major advantage of the use of clusters is that they are small enough those usual chemical analysis methods such as liquid NMR spectroscopy and single crystal X-ray diffraction for their analysis. Metal oxides materials are interesting class of chemical materials beside pure metal clusters and nanoparticles, because their interesting structural, electronic and magnetic properties often paired with low toxicity. Silica or spherosilicate both have in common that the surface contains reactive oxygen groups that can be used for further functionalization. Mono-functional polyhedral silsesquioxane (POSS) ($R'R_7Si_8O_{12}$) (where, R' = functional group, R = nonfunctional group) are prepared by reacting the incompletely condensed molecule $R_7Si_7O_9(OH)_3$ with $R'SiCl_3$, and a variety of functional organic groups R' can be introduced, such as vinyl, allyl, styryl, norbornadienyl, 3-propyl methacrylate, etc (Fig. 12a). While the formation of the inorganic building systems is still costly because of the low yields products, another building block is much easier to produce, namely spherosilicates [52,94].

The polyhedral silicate species $[O-SiO_{3/2}]_n^{n-}$ are usually prepared by hydrolysis of tetraoxosilicate $Si(OR)_4$ in the presence of quaternary ammonium hydroxide (Fig.12b). Spherosilicates are produced from sources of inorganic silica and can be considered the smallest piece of silica (Si—O—Si).

Recently the modification and dispersion of transition-metal oxide clusters and particles has become more and more important, due to their

catalytic, stability, magnetic or electric properties [95,96].

However, the surface functionalization of the clusters by stable connected with organic groups is preferred with surfactants. There are two methods can be used for such a modification: either a cluster or particle is prepared in a first step and the surface is subsequently modified, or the surface functionalization is obtained in situ during the preparation. The cluster or nanoparticle is formed in a first step and the functionalization with organic groups is applied in a second step. Reactive surface functionalizations are required for allowing the chemical reaction with the surface decorating molecules, as in the nucleophilic substitution reactions (silica-based building blocks typically surface OH-groups are reacted with so-called silane (Si-OH) coupling agents to form stable covalent bonds. These molecules contain reactive Si-Cl or Si-OR groups that react with surface silanol (Si-OH) groups to form stable siloxanes (Si-O-Si) bonds. Another way to attach functional groups to the surface of a preformed building block is the exchange of surface groups. Organic groups can also be attached to the cluster surface by chelating or bridging ligands via coordinative interactions on metal oxide clusters or such as particles are carboxylates, sulfonates, phosphonates, β -diketonates, etc. These groups may carry organic functionalities, such as polymerizable double bonds.

9.1.2. Organic building blocks

Organic building blocks (Polymerizable Organic Groups) can also be used for the formation and modification of hybrid materials such as oligo- and polymers as well as biological active molecules like enzymes [97,98].

The origin of hybrid materials is the modification of inorganic networks with small organic molecules as sol-gel derived silicon-based materials. There are different kinds of alkoxides which connected to functionalize the organic group, such as (vinyltrimethoxysilane, VTMS), epoxy (3-glycidoxypropyltrimethoxysilane, GPTMS) or methacrylate (3-methacryloxypropyltrimethoxysilane (MPTMS)). Often the nanocomposites are formed by simply mixing the two components, where the end groups of polymeric chain can be used for an interaction with metal clusters or particles. Organic molecules with hydrolysable alkoxysilane or chlorosilane groups, organic dyes, optical groups, or

switchable groups are molecules which have been used to prepare hybrid organic-inorganic nanocomposites. Oligo- and polymers as well as other organic macromolecules show different solubilities in specific solvents compared with their monomers; usually the solubility of the polymers is lower than the monomers. However, many preparation mechanisms for hybrid materials and nanocomposites are based on solvent chemistry, for example the sol-gel process or the wet chemistry formation of nanoparticles. So, if homogeneous hybrid materials and nanocomposite materials are targeted, an appropriate solvent for both the inorganic and the organic macromolecules is of great benefit. For example, many macromolecules are soluble in Tetrahydrofuran (THF) as an industrial solvent for polyvinyl chloride (PVC) and in varnishes, which used as co-solvent in aqueous solution [99].

The hybrids which result from this class of alkoxides may contain an organic polymer whose extent depends on the synthesis conditions for production.

9.1.3. In situ formation of the components:

During this process the hybrid nanocomposite materials is based on the chemical transformation of the used precursors. For example, if organic polymer matrices are formed and the sol-gel route is used to produce the inorganic materials. In these cases, well-defined separate molecules are transformed to (2D and/or 3D) dimensional structures, with totally various properties from the original components. So, changing one parameter and the control over the sol gel process can often lead to two very different materials. As example, silica nanoparticles formed by the sol-gel method, the change from base to acid media cases a large difference because base catalysis leads to a more particle-like microstructure while acid catalysis produce a polymer-like microstructure. Where, that the final performance of the produced materials is strongly dependent on their processing and its optimization conditions. Chang et al. [89] prepared zirconia single crystal containing pore's structure using sol-gel-hydrothermal route. The unique character of the prepared particles is the presence of irregular pores that are embedded within the single crystals [100].

During the thermal treatment the amorphous gel transferred into the crystals and some pores are coarsened with the crystal's growth. The small pores were appeared because gaseous hydrolysates of

urotropine were linked in the gel during the thermal treatment [101].

10. Sol-gel process of hybrid organic–inorganic naocompsites based on polysilsesquioxanes.

Silsesquioxanes (SQs: $\text{RSiO}_{1.5}$), is class of the materials containing Si–O framework, contain the various functional groups as side chains (R) and are inorganic materials indicating the compatibility with organic materials such as polymers [102].

These materials having superior chemical, mechanical, and thermal properties derived from Si–O framework with high bond energy compared with C–C bonds [103].

Polysilsesquioxanes (POSS) is a class of hybrid organic–inorganic materials that have the basic repeating unit of $[\text{RSiO}_{1.5}]_n$. These materials can take various forms and used in different applications due to the combination of the siloxane bond networks with organic constituents. So, polysilsesquioxanes-base materials used to protect stonework from the ravages of weathering, encapsulate fluorescent organometallic compounds in oxygen and carbon dioxide sensors and as nanoscale filler for advanced composites [104].

The polyhedral oligomeric (POSS) PSQs are prepared by polycondensation reaction of the trifunctionalsilane monomers such as organo trialkoxysilanes and organo- trichlorosilanes. Generally, these multifunctional monomers result in the production of insoluble polymeric molecules with irregular three-dimensional structures of Si–O–Si bonds. Where, the regularly structured poly (PSQs) has only been obtained in the limited cases. While the produced power from this method for introducing organic groups into hybrid materials is clear, very few researchers realize the extent to which the nature of the organic group will determine the course of sol–gel chemistry being used [105].

The versatility of SQs gives good and easy control over the sol–gel polymerization process and the ultimate properties of the final hybrid organic–inorganic materials.

The obtained end product is depending on the monomer type, its concentration, the pH value of the solution, the ratio of water, type and amount of catalyst, the identity of the solvent and reaction temperature. The basic building block consists of repeating unit or monomer is tetra-coordinate silicon

with three siloxane bonds and an organic substituent [106].

The control on the preparation of supramolecular organic–inorganic hybrid materials (highly-ordered structures) is evident that the development of PSQs with regularly controlled molecular and higher-ordered structures is one of the important parts for research fields of SQs.

Kaneko and co-workers [107] have investigated a preparation process for ammonium group containing PSQs with controlled molecular and higher-ordered structures using the sol–gel method through the hydrolysis and polycondensation of organotrialkoxysilane (organotrimethoxysilanes) monomers containing amino groups in aqueous inorganic acids and hydrochloric Acid under stirring for 2h at room temperature, to form 3-aminopropyltrimethoxysilane (APTMO) PSQs, as followed by heating (50–60°C) in air until the solvent was completely evaporated. Forming $(\text{PSQ-NH}^3+\text{Cl}^-)$ hexagonally structures with higher-ordered structure.

Marcelo et al. [108] prepared and hybrid organic–inorganic epoxy-copolysilsesquioxane by sol gel method using 3-aminopropyltriethoxysilane (APTES) and phenyltriethoxysilane (PTES) precursors incorporated in epoxy resin based, improved with multi-walled carbon nanotubes (MWCNT). The produced hybrid nanocomposites presented enhancement on thermal stability, exhibiting decay temperatures higher than 340°C with N_2 and show a moderate enhancement of the mechanical properties.

11. Hybrid organic-inorganic particles

Hybrid organic-inorganic particles are an important class of hybrid materials with particle size ranging from 10 nm up to several 100 nm with wide range of applications from the encapsulation, controlled release of active substances to use as fillers for the paint and coating industries. Hybrid organic-inorganic particles can be defined as colloidal particles that contain both organic and inorganic domains. The organic and inorganic components can form either two clearly distinguishable macroscopic phases such as in composite particles, or exhibit some degree of phase mixing at the molecular level such as in hybrids. Nowadays, colloids cover a wide range of different materials and are currently defined as two-phase systems in which particles of colloidal size

(from 10nm to 1 μ m) of any nature (e.g., solid, liquid or gas, organic or inorganic) are dispersed in a continuous phase of a composition or state. In a colloidal suspension (sol) each particle consists of a large number of molecules or "molecular aggregates" stabilized in solution by chemical bonds or electrochemical means (Fig.18). According to their small size and stabilization, they remain dispersed for a long time and also have the property to scatter light (so-called Tyndall effect) (Tyndall scattering defined as light scattering by particles in a colloid or particles in a very fine suspension) [109].

The physicochemical method for preparation of organic-inorganic particles involves interaction of preformed polymeric materials (macromolecules and/or nanoparticles with particles templates, where the particles and organic phases are generated in situ in the presence of organic or inorganic particles, respectively. Actually, owing to their small size, colloids are nearly all surface! Not only are surface phenomena accentuated in colloidal materials but physical confinement due to boundaries effects creates strong size-dependent properties and their large surface area also prone to adsorb large amounts of chemicals, which is largely responsible for their stability in solution and also allows introducing different types of molecules on their surface.

These particles can be divided into three groups according to the method which has been used for their preparation:

1. **Organic-Inorganic** colloids can be constructed by assembling organic and inorganic components (particles or macromolecules) which elementary units (or bricks) forming the building blocks of the resulting hybrid colloid,
2. **Organic-Inorganic** colloids can be produced in situ by polymerizing organic precursors in the presence of preformed inorganic particles and,
3. **Organic-Inorganic** particles can be obtained by continuously reacting inorganic and organic molecular precursors.

To solve the problem of liquid PEG leakage, a novel kind of shape-stabilized composite phase change material (ss-CPCM) based on PEG and a carrier matrix was modified. The powder and organic-inorganic composite (ss-CPCMs) can keep its solid state even the phase-change substance is changed from solid state to liquid state. Where, the carrier matrixes can make liquid PCMs and protect PCMs from harmful interactions with the surrounding materials and environment. So, Qian et

al.[110] prepared a novel polyethylene glycol (PEG)/SiO₂ shape-stabilized composite phase change material (ss-CPCM) with the 'hazardous waste' oil shale ash and PEG used as the phase change material for thermal energy storage, SiO₂ acts as the carrier matrix to provide structural strength and PEG was impregnating into silica-gel porous network structure.

The sol gel formation of PEG/SiO₂ss-CPCM by the hydrolysis and condensation using sodium silicate without surfactant or co-solvent. Where, the silica sol was prepared at 60°C and using acetic acid addition in the (Step1) until the pH \approx 10.85, as presents in the schematic (20). At the pH value 10.85, the hydrolysis reaction of sodium silicate solution began to transform into silica sol up to the pH value and the sol solution as encapsulation precursor was obtained. Then the PEG (melted) was dropped into the previous silica sol under continuous stirring. In step 2, the silica gel /PEG nanocomposite was obtained at the temperature rose from 60 to 70°C and pH value was adjusted to 4–5 by acetic acid and three-dimensional gel network was obtained.

12. Organically modified sol-gel glasses (ormosils)

Basically, the sol in the sol gel process gradually transforms towards the formation of a gel network structure containing both a solid phase and a liquid phase in the same prepared matrix. The precursors used in sol-gel processing consist of a metal or metalloid element surrounded by various reactive ligands forming metal alkoxides, such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), triethylphosphate (TEP), aluminates, titanates and zirconates, are the most popular precursors because of their high reactivity towards water [20,69].

The introduction of different organic groups through inorganic alkoxide matrix has led to organically modified sol-gel glasses, known as ormosils. Organically modified silica-based or organically modified silicate (ormosils) are one type of organic-inorganic hybrid nano-materials. Nanoparticles have been prepared from silica precursors modified with various organic functionalities such as ethyl, methyl, vinyl and phenyl modified silicas have been synthesized for using these particles as modifiers for polymers and polymer matrix composites. Ormosil nano-materials have attractive features compared to inorganic sol-gels. In first, they allow specific binding for different drugs molecules such as enzymes and antibiotics to the silica network,

for example on silica grafted with aminosilane-glutaraldehyde to an amine bearing enzyme. Second, they allow the encapsulation of catalysts with the organic molecules, or enhancement, the covalent bonding of a charge transfer cofactor to the composite material via a chemical reaction with the previously grafted groups. And they make it possible to control the wettability of organic-inorganic composite material by an adjusting of the ratio of chemicals monomers [111], tetraethoxysilane (TEOS) and ormosil monomer structures and ormosil formation. The organic modification matrices are employed to slow the degree of cross-linking, which improve film adhesion to its support, reduce the concentration of surface silanol (Si-O-H) groups and the capacity of ion exchange and incorporate reactive groups that can be used for establish molecular recognition species on pre-prepared xerogels. The variation of the number and type of organic moieties connected on the silicon monomer that produces a variety range of pore sizes which can be created in the ormosil network [112].

The mechanical and optical properties of sol gel glasses, can be improved using modified alkoxide precursors $\text{RSi}(\text{OEt})_3$ to create organic-inorganic hybrid composites. Where, the covalently bound organic groups (ethyl, methyl and vinyl) decrease the effect of mechanical tension during the drying process. In order to overcome the phase separation in ormosils, functionalized alkoxides (F-R-Si (OEt)₃), where F is a functional group as amino or isocyanate and R' is an alkyl spacer, are usually used to as a covalently dopants in the matrix.

After drying the inorganic-organic hybrid xerogels, appears optically clear and dense. The reactive area of ormosil (organic modified sol gel materials) can be determined by its wettability (the ability of a liquid to contact with a solid surface, producing from intermolecular interactions), which can be increased by incorporating solvent/water soluble components such as polyethylene glycol (PEG) in the systems and dissolving them out by immersing the electrodes in an electrolyte solution [56].

By changing the ratio of tetraalkoxysilane (TEOS) to organotrialkoxysilane (OTOS) can control the cation exchange capacity and polarity of porous surface. The addition of various polymers such as poly (ethylene glycol) (PEG) or poly(vinylalcohol) to tetraethoxyorthosilicate (TEOS) and organosilane-

derived sol-gel material offers improved material properties such as optical clarity, dehydration and rehydration stability, results in the enhancement of the stability for entrapped lipase when compared to entrapment without polymer additives. Processes such as ageing time, drying, chemical stability and densification effects the sol-gel materials, which are related to the kinetics of rates of hydrolysis and polycondensation, temperature, condensation electrolyte (acid/base), solvent nature and alkoxide precursor type that determine the structure of the gel [113,114].

The particle sizes of the sol and the cross-linking of the particles depends on the pH, the ratio of $[\text{H}_2\text{O}/\text{Si}(\text{OR})_4]$ and solvent play an interested role in the kinetics of gelation, which can be either acidically or basically catalysed. The time of gelation has affected by the water contents, low water content, where the higher water content increases the gelation time with the increasing the water contents. It is known that the biomolecules are highly sensitive and fragile in nature; hence their carrying media should be mild and closer to the native environment after immobilization. Sol-gel inorganic matrices are low biocompatible, hence the organic modification for sol-gel starting materials may supplying good way of controlling the nanoporous geometry of ormosil suitable for sensor design.

13. Organically modified ceramics materials (Ormocers).

Ormocers are belonging to the class II of hybrid organic-inorganic materials, where the organic and inorganic molecules at nanoscopic scale are bonded through strong chemical bonds. Ormocers as hybrid materials have been modified as an excellent alternative to the dimethacrylate based composites. Ormocers nano-materials were fabricated in an attempt to overcome the problems created during the polymerization shrinkage of traditional conventional composites because their thermal coefficient expansion is very similar to natural tooth Structure [115].

Ormocers are classified as 3D- cross-linked copolymers with nano-ceramics high polymerization opportunities that allow ormocers to cure without leaving a residual monomer, thus having better biocompatibility with the tissues. Ormocers are classified between inorganic and organic polymers and have an inorganic particle and an organic network. So, the monomers are will-embedded in the

matrix what reduces the release of monomers. The chemical structure of these nanocomposites is based on the organically modified metal alkoxides and functionalized organic-inorganic polymers. An inorganic (Si-O-Si) three structural network is produced through targeted hydrolysis and inorganic poly-condensation in a sol-gel process. The inorganic continues poly-condensation and organic polymerization lead to the fabrication of an inorganic-organic co-polymer. The inorganic components for ormocers materials are bound to the organic polymeric materials through multifunctional silane molecules. After polymerisation the organic portion of the methacrylate groups form a three-dimensional network. The resulting ormocers nanomaterials are highly transparent in the visible wavelength regime, having better thermal and mechanical properties, high chemical stability and resistance, and they produced at low cost. Effectively the ormocers as a new class of organic-inorganic nanomaterial combines the high surface area properties of the silicones (Si-O-Si), the toughness of the polymeric materials and the hardness and thermal stability of ceramics. The organoalkoxysilanes modified with active groups such as vinyl, amino and epoxy have been employed as starting precursors to prepare hybrid organic-inorganic nanocomposites [116].

Besides, the hybridization with other polymerizing molecules, they are polymerized to comprise polyethylene-type C—C skeletons and Si—O—Si networks. For the synthesis of modified hybrid materials based on organically modified silicon alkoxides, there are various methods are described in the literature: sequential syntheses, syntheses issued from multi-functional alkoxysilanes, and syntheses from alkoxysilanes functionalized by a polymer.

About the sequential synthesis is separated two parts: the first one consists in the preparation of an inorganic structure by condensation reactions of the alkoxysilanes moieties, while the second part is the organic cross-linking by photochemical or thermal curing leading of the formation of materials referred to as ormocers [117].

The formation processes based on poly-functional alkoxysilanes are used to synthesize hybridorganic-inorganic composites from organically modified silicon alkoxides. Ormocers matrices were used for commercially available multi-applications Admira, Microelectronics as in a complete Pentium™ multi-chip module (133 MHz) was realized, flexible

substrates as in optical waveguides and in industrial applications for micro-optics through combining UV lithography and softembossing, micro-optical elements, for example the replicated microlenses [118].

14. Characterization of hybrid organic-inorganic nanocomposites

The wide range of characterization methods used in the analysis of the materials' compositions, the molecular and nanometer structure as well as the physical properties, therefore a complete list of these techniques.

14.1. Nuclear magnetic resonance (NMR)

Liquid state NMR techniques are good powerful tool in the characterization of solutions, that it is a very sensitive technique for the chemical environment of nuclei can be investigated, which makes it also an interesting technique for solid materials. With the large variety of nuclei which can be applied as probes in solid state NMR due to their NMR activity, and the interesting nuclei for hybrid organic-inorganic materials such as C, Si, V, Al, Sn, P, F and many others. But the most measured nuclei in the field of hybrid materials are ²⁹Si. ²⁹Si NMR is a tool in the determination of the proportions of different silicon molecules in sol-gel based nanomaterials and understanding of its fundamental parameters, (precursor structure and reaction conditions).

14.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is analytical tool for surface sensitivity used to examine the electronic state on the surface and the chemical compositions of the prepared sample. Where, the examiner sample is placed under high vacuum and is bombarded with X-rays which penetrate into the top layer of the sample (~nm) and excite electrons. The kinetic energy of the emitted electrons binding energy of the ejected electron can then be determined from:

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$$

where ϕ gives the work function of the material.

14.3. Scanning electron microscopy (SEM)

Is analytical tool with high resolution images for the surface of the prepared sample. SEM is good for judging on surface structure; because of the SEM images have a characteristic 3-D appearance.

14.4. Transmission electron microscopy (TEM)

TEM images are produced by using a beam of electrons onto a very thin specimen which is partially transmitted by those electrons and carries information about the inner structure of the specimen. The image is recorded on fluorescent screen (CCD) camera, which displayed the image on computer. Sometimes the organic systems of the sample are not well detected because they decompose in the electron beam; this can be overcome using cryogenic microscopy, which keeps the sample at liquid nitrogen or liquid helium temperatures (cryo-TEM).

14.5. Atomic force microscopy (AFM) Atomic force microscopy

Recently, AFM became a very important analytical tool for description the surfaces and nano objects. Their method is simple; a cantilever with a sharp tip at its end, typically composed of silicon or silicon nitride with tip sizes on the order of nanometers is brought into close proximity of a sample surface. The van der Waals force between the tip and the sample leads to a deflection of the cantilever. Typically, the deflection is measured applying a laser beam, which is reflected from the top of the cantilever into an array of photodiodes. AFM technique has several advantages over other nano analysis tools, such as the electron microscope. Contrary to other methods AFM provides a 3-D surface profile of a sample.

14.6. X-ray diffraction

X-ray diffraction is used to identify the formed different phases in a polycrystalline material. There are two important advantages for analysis of hybrid materials by XRD is that it is fast and nondestructive. and the X-ray pattern is fingerprint and mixtures of different crystallographic phases can be easily distinguished by comparison with reference data. If the crystallites of the powder are very small the peaks of the pattern will broaden. From the broadening of the peaks in XRD the pattern it is possible to determine an average crystallite size by the Debye–Scherrer equation:

$$d = k\lambda / B \cos\theta$$

where k is a factor, 0.9, λ is the wavelength of the X-ray radiation, B is the broadening of the diffraction line and θ is the Bragg angle.

14.7. Fourier-transform infrared spectroscopy

FTIR spectroscopy is one of the most important spectroscopic analyses techniques used for organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The FTIR spectroscopic technique is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption positions are generally presented as either wave numbers (ν) or wavelengths (λ). Wave number defines the number of waves per unit length. Thus, wave numbers are directly proportional to frequency, as well as the energy of the IR absorption. The wave number unit (cm^{-1}) is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy.

14.8. Thermal analysis techniques

Thermogravimetric analysis (TGA) is the tool concern for studies the

weight changes of samples in relation under the changes in applied temperature. TGA is employed for hybrid organic-inorganic materials and nanocomposites to investigate the thermal stability (degradation temperatures), the amount of inorganic component, which usually stays until the end of the measurement due to its high thermal resistance, and the level of absorbed moisture in these materials.

Differential scanning calorimetry (DSC) is a thermoanalytical technique that compares the difference in the amount of heat required to increase the temperature of a sample and a reference with a well-defined heat capacity measured as a function of temperature.

15. Applications

15.1. Hydrogels for medical applications

15.1.1. 'On-Off' drug delivery systems

In the last decades, smart hydrogels have received great interest owing to their exceptional promise in biomaterial applications such as drug, protein, cell

delivery, wound dressing and tissue regeneration [119].

Drug delivery systems must be well-designed with the control solute release over time. The hydrogels appear two clear advantages: (1) The rate of drug release can be controlled in different ways such as by changing the crosslinking density, preparing the hydrogel with various monomers, or controlling the ratio of hydrophilic to hydrophobic monomers. (2) Hydrogels may interact less strongly with drugs; consequently, a larger fraction of active molecules of a drug, especially proteins and peptides, can be released through hydrogel carriers. The 'on-off' drug release in response to smaller temperature changes between 36 and 38 °C was also achieved, as demonstrated in [120].

15.1.2. Injectable hydrogels and tissue engineering

The sustained-release medication is to place the drug in a delivery system and inject or implant the system into the body tissue is consider one of the most obvious ways to provide[121].

Tissue engineering technology has emerged for the design of an ideal, responsive, living substitute with properties similar to those of the native tissue [140]. Scaffolds engineering are basically 3D structural materials that enhancement cell adhesion, migration, differentiation and provide guidance for new tissue formation. Hydrogels is interested useful scaffolding biomaterials as they nearly resemble the natural tissues. Cell technology using the smart hydrogels provides a promising therapeutic modality for diabetes, hemophilia, cancer and renal failure [122].

15.2. Porous hybrids for tissue engineering scaffolds and bioreactors

The ability of materials to promote and understand the cell culture is applied for tissue engineering and bioreactors. The engineering of bioreactors requires porous materials that are chemically stable and better affinity for the pertinent cells.

15.2.1. PDMS–silica porous hybrids for bioreactors

The porous ormosil (TEOS-PDMS (poly(dimethylsiloxane))) hybrids are chemically stable and uniform pore size, while their biological activity is controllable such as incorporating calcium ions or other physiologically active centers in their

matrices. The porous Ormosils hybrid derived from sols in which calcium ions are embedded are bioactive systems enough to deposit apatite on their wall surfaces. The introduction of ormosil hybrids covered pore walls of a porous and they have excellent cell-attaching ability, which makes the Ormosil hybrids promising materials for biomedical scaffolds.

15.2.2. Chitosan–silicate porous hybrids for scaffold and drug delivery applications

The hybridization of some natural polymers such as chitosan and gelatin as polysaccharides increase their chemical stability [123].

In addition, bone tissue scaffolds are required to be osteo inductive (is the process or ability of material to induce stem cells to differentiate into bone cells) or osteo conductive. Osteo induction (is the process whereby osteogenic cells in porous material (grafts also) differentiate into bone cells or form bone tissue). For example, when a bone tissue defect is coated or filled with granular scaffold materials, the defect should be covered with a piece of membrane that embed the granules in the defect, and keeps fibroblast from coming into the defect. Chitosan and chitin are the most candidates for drug carriers because of its biodegradation, nontoxic and biocompatibility, while various classes of drugs are attempted, including antihypertensive agents, anticancer agents, proteins, peptide drugs, and vaccines. When dosing a drug to a patient, the drug is to be rigorously released to increase the concentration in blood immediately up to a threshold value. Then, it is continuously released to keep the concentration almost constant.

15.3. Hybrid organic-inorganic materials for dental applications

The hybrid nano-composites are used as filling composites in various dental applications due to their properties such as hardness (quickly under the effect of blue light), low effect with PH value, elasticity and thermal expansion behaviour. Besides, these hybrid materials are easy to use by the dentist, low shrinkage degree, are non-toxic and non-transparent to X-rays. The sol–gel process based on organic reactive monomers for the formation of an inorganic network, and then polymerisation takes place with less shrinkage and subsequent curing process, enhanced by the existing inorganic Si–O–Si network.

15.4. Hybrid organic-inorganic Materials for bioactive applications

Bioactive organic-inorganic hybrids materials find applications in the field of biotechnology as a biosensors and bioreactors. Livage et al. [124] loaded the high activity of enzymes, antibodies or micro-organisms on or in solid substrates in order to be reusable and protect them from denaturation to perform specific reactions.

Currently, active-centers are incorporated in natural and synthetic polymers (polysaccharides (chitosan and chitin), polyacrylamides, alginates, etc.) used for bio-immobilization via covalent binding or entrapment. Where these organic-inorganic matrices exhibit better mechanical strength together with improved chemical and thermal stability, and don't swell in most solvents preventing the leaching of entrapped bio-molecules. For example, nucleic acid biosensor, based on a polyacrylamide/aptamer hydrogel, was improved for detection of small molecules such as adenosine and cocaine [125,126].

This hydrogel biosensor was modified by two DNA strands that were crosslinking with an aptamer linker. Another type of biosensor, Emregul et al. [126] prepared novel highly sensitive electrochemical carboxymethylcellulose-gelatin-TiO₂-superoxide dismutase biosensor on a Pt electrode surface, which play an important role in cell protection mechanisms against oxidative damage (harmful interaction with biological molecules) from reactive oxygen species (O₂^{•-}). The developed biosensor appears high analytical performance with a wide linear range, high sensitivity and fast response time.

15.5. Hybrid organic-inorganic nanocomposites for proton-exchange membrane fuel cell (PEMFC) applications.

The fuel cell core efficiency and durability based on the proton exchange membrane (PEM) by allowing the proton transport from the anode to the cathode, which is an electron non-conductive material and to act as a gas separating barrier (H₂, O₂). The principal functions of PEM are therefore proton conductor, fuel barrier, and physical separator between the anode and cathode, but the PEM needs to be chemically (highly acidic medium) and thermally (from 80°C to 140°C) stable. The organic membranes are synthesized of organic polymers containing acidic groups such as sulfonic, carboxylic or phosphonic

groups which dissociate when solvated with water, allowing H₃O⁺ hydrated proton transport. So, the performance of the membrane is related to the ionic group concentration and to the hydration rate. The advantages of direct methanol fuel cell (DMFC) such as high energy density, quiet operation, without requirement of fuel reforming process, and environmental friendliness are made (DMFC) promising energy conversion device for portable devices or transportation applications [127].

During the operation of DMFC, operating with methanol as fuel feed, is oxidized at the anode to produce protons and electrons. The resulting protons are transported through a membrane and react catalytically with oxygen to produce water at the cathode, whereas the electrons are transported through an external circuit to generate electric energy. As a fuel barrier, PEM must have low methanol crossover. In this regard, Bai et al. [127] enhancing the proton conductivity by using chitosan membrane to work as proton exchange membrane for direct methanol fuel cell.

Where, the nanotubes carrying sulfonate polyelectrolyte brushes are synthesized by the polymerization process and then embedded into CS polymeric matrix to fabricate nanohybrid membranes. The results nanotube/ CS long polyelectrolyte brush allows SHNTs to construct continuous and wide pathways, along which sulfonic acid-amide acid-base pairs are formed and work as low-barrier proton-hopping sites, imparting an enhanced proton transfer.

15.6. Hybrid organic-inorganic nanocomposites as adhesives nanocomposite

The field of sol-gel derived hybrid nanomaterials for adhesives application, for example the organically derived siloxane resins. They are made of sol gel SiO₂ units cross-linked with trimethylsiloxy or hydroxyl groups [42].

Their various application concerns the pressure-sensitive adhesives, cosmetics, water-repellents and additives for paper coatings. Polyethylene polymer is accepted as a wire and cable insulation material, because of their desirable balance of electrical, mechanical and processing properties. Another application for the adhesive hybrid materials derived siloxane-polyethylene hybrid polymers were used to fabricate thermoplastic equipment in the automotive industry. The barrier systems made from hybrid nanocomposites has been interested as a result of the

requirements to develop much more sophisticated materials in fields such as solar cells, optics, electronics, food packaging. The modified hybrid inorganic–organic coating for a whole encapsulation system since apart from the physical encapsulation it acts as an adhesive/sealing layer barrier against water vapour and gases, as well as an outside layer for weather ability. The flexible nature of this hybrid material results in an optimized encapsulation process and especially in good protection of the edge area, the most difficult part for protection.

15.7. Hybrid organic-inorganic materials for optical applications

The formation of organic–inorganic hybrid networks for optics, photonics and opto-electronic should be directed to different specific purposes as the materials incorporate or does not incorporate optically active external centers (metal ions (TMs AND REs) or organic molecules. The synthesis strategy has been based on the optical transparency and the control of the index of refraction. Optically active hybrids: The synthesis strategy for materials lacking metal activator ions the strategy has been essentially directed towards the reduction of groups responsible for quenching of the luminescence (e.g. silanol (Si—OH) groups, residual solvent, etc.). For hybrids doped with metal activators, the focus is the encapsulation of the emitting centers with their protection from nonradiative decays by the organic–inorganic host itself favoring potential energy transfer processes. The organic molecules can be dispersed and separated from each other, thus reducing intermolecular quenching of fluorescent features [36,48]. For examples some representative rare earth ions-doped organic dye-doped hybrids matrices.

15.8. Hybrid materials for photochromic and photovoltaic devices

Photochromism is defined as the reversible photocoloration (photochemical reaction) of a single chemical species between two states having different absorption spectra, that result from the action of electromagnetic radiation in one direction at least, but in essence there is no dividing line between photochromic reactions and other photochemistry. Photochromic hybrid organic–inorganic nanocomposites have great attention due to their different application in photoactive devices as optical memories, windows, photochromic decorations, optical switches, filters or non-linear optics materials.

There is growing development in photochromic hybrid materials for the purpose of improving existing materials and exploring new photochromic hybrid matrices. The most commonly used method for design and formation of photochromic hybrid materials based on the introducing of organic molecules (polymeric materials) in organic–inorganic matrices is the sol–gel process. The spectacle lenses prepared from organic polymers are an assembly of molecules, elementary units constituted by a core and electrons. The difference between these two energy levels can be recorded using a spectrometer which gives a graphic representation known as the absorption or transmission spectrum.

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