HYBRID NANOCOMPOSITE MATERIALS

1. Introduction

When it comes to trying new combinations in order to get materials with desired properties human technologist have shown a very long tradition in the making of daring blends. Mixing dissimilar components proved most useful in the hands of adobe artisans who discovered how straw could substantially improve the drying process of clay bricks avoiding dreadful cracks. In a similar way and as a worthy heir of this “adobe approach”, modern technology provides us with composite materials such as fiberglass-reinforced epoxy resins in which the dispersion of the inorganic fibers within the polymer leads to materials with improved mechanical properties and wider structural applications. Other chemical industries like those manufacturing paints and coatings or the polymer industry also mix organic and inorganic components in order to get optimal formulations (inorganic pigments with organic solvents and surfactants, inorganic fillers with polymers etc).

But in recent decades scientists and technologists have begun to realize that there is more to composite materials than just playing with mixtures.

As the particle size of the components in a composite material is reduced, their interface increases, with its area increasing proportionally to the reduction in particle size for a given amount of material. An increased interface/bulk ratio leads to a growing relevance of the interface in determining the properties of the composite, but with each of the components still keeping its own identity as separate phases. Yet, as the degree of dispersion increases further and the components reach nanometric dimensions we get into a twilight region in between physical mixtures and chemical compounds, the realm of nanocomposite materials. At that point, composite materials break into a new dimension, a chemical dimension.

As a matter of fact, nowadays we can distinguish two major approaches for the development of nanometric structures and nanocomposite materials. A downsizing approach, which strives to reduce and keep reducing the particle sizes of bulk solid materials until their properties reach quantum effects, and an upsizing approach, which starts with statistical bundles of quantized atoms or molecules and aims at assembling ever-growing atomic or molecular ordered clusters with cooperative properties.

1.1. Cross-Breeding of Materials.

It is in this chemical realm of nanocomposite compounds that hybrid materials thrive. In this case, *hybrid* refers to the mixed nature of the composite, normally made of dissimilar organic and inorganic components, each with characteristic chemical properties but interacting so closely that they frequently form a single phase. In combining organic and inorganic components, materials scientists can get the best of two worlds. But they can get more than that, because in certain cases these combinations present properties that are superior to the simple combination of properties from the components, ie, they present a synergic behavior.

Indeed, being composed of an organic and an inorganic part has turned out to be the most common case among hybrid compounds and the term hybrid has become almost synonymous of organic–inorganic combinations; but taken in a wider sense, certain combinations of dissimilar inorganic–inorganic as well as organic–organic compounds could also be properly considered within the category of hybrid materials and we will see some examples of this later in this article.

1.2. From Ancient Pigments to Future Microelectronics.

Although the understanding of their intimate chemical structure has not been possible until very recently, the chemistry of truly hybrid materials can be tracked back many centuries.

Maya artisans working in the eight century AD in Mexico and Central America could have never suspected they were making a glorious hybrid material by mixing (probably inadvertently) a deep blue pigment from the organic kingdom with a white clay from the inorganic world. But in washing indigo with palygorskite-carrying waters and then drying the mixture, they had found a pigment able to display all blue-green hues of the Caribbean Sea and able to endure many centuries in a harsh environment (Fig. 1).

Since prehistoric times human kind has probably come across many fascinating hybrid materials, from natural ones like bone to artificial ones like Maya Blue. But only in the second half of the twentieth century has it been possible to begin understanding the intimate chemical nature of these complex materials and with understanding comes control.

In the last 20 years, taking the interface between organic and inorganic materials as a land of opportunity, chemists willing to deal with complex systems at the borderline between molecules and polymers have led to an explosive

Fig. 1. Mayan Blue Reprinted with permission from Refs. 1,2.

growth in the understanding and control of the chemistry of hybrid materials that can now be designed for specific purposes and applications. The variety of these materials is overwhelming, both from the point of view of their chemical nature as well as from their possible applications. Furthermore, note that the field of hybrid materials has grown parallel to the design of nanocomposite and nanostructured materials (3), since most of the hybrid architectures that will be described in detail below have the organic and inorganic phases interacting at a molecular nanometric level (4). The reader is referred to the chapter of this encyclopedia by Vaidaya and co-worker on this related topic (3). This makes of hybrid organic–inorganic materials key structures for the development of nanotechnologies and nonodevices.

The initial thrust in the chemistry of hybrid organic–inorganic materials came from research on intercalation and grafting chemistry (5), and later from sol–gel materials (6,7) for the development of novel carbon–silicon networks that could be used as improved structural materials, something in between glass and plastic (8), but soon it was realized that the hybrid approach could also be used with great advantage for the design of functional materials. Nowadays research and development of hybrid materials span combinations that harness chemical and biochemical activity, electrochemical or photochemical properties, as well as magnetic, optical or transport properties in materials formed by organic or inorganic matrices and molecular, polymeric, or crystalline species. In this article, we will try to summarize the chemical richness of these materials and the myriad applications they are finding, from already commercial structural materials to future electroionics.

Among the many possible criteria to classify a large family of compounds, we have chosen two major ways to classify hybrid materials in order to structure this article and facilitate retrieval of information on the topic; namely, a chemical classification, according to composition, and a technical classification by properties and applications.

2. Types of Hybrids According to Chemical Criteria

From a chemical point of view, hybrid materials can be broadly classified according to the nature of the matrix phase or predominant compound. In this respect, the literature is not consistent. Many researchers talk about organic–inorganic materials in a generic way, regardless of whether the organic or the inorganic phase predominate, and even when distinctions have been made, no common criterion has been adopted. Here we will use an arbitrary short-hand notation to facilitate the analysis of related groups of materials. Depending on the dominating structural matrix, we will distinguish and analyze organic–inorganic (OI) and inorganic–organic (IO) hybrids. Thus, we will refer to *OI* materials or compounds to denote hybrids where the *organic* phase predominates and constitutes the matrix where an inorganic species is inserted or dispersed, whereas *IO* materials will be those with *inorganic* matrices and integrated organic "guests" (Fig. 2). The term "*organic–inorganic*" (without initials) will be used when referring generically to hybrid materials. Obviously there will be borderline cases not conforming to any of this two types of hybrids, materials made, eg, by the

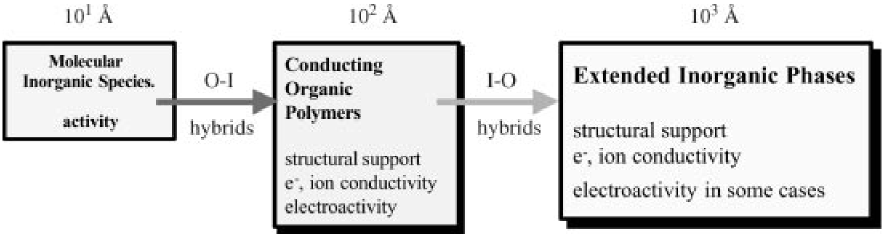


Fig. 2. From the point of view of their molecular dimension, conducting polymers occupy an intermediate position in between monomeric molecules and extended solids. This allows for the isolation of organic–inorganic hybrids, where molecules are dispersed within COPs, and inorganic–organic hybrids, where COPs are inserted within extended solids. Here we will apply this notation to hybrids in general to facilitate analysis and discussion of related materials.

combination of two or more dissimilar components organized as nano-sized particles or domains, each conserving its own chemical nature. We will also discuss these "polyphase" hybrid nanocomposite materials (denoted as **NC**) and will analyze similarities and differences with their monophase hybrid counterparts.

Another classification commonly accepted that will also be used throughout this chapter, centers on the *type* of chemical interaction at the interface between the components of a hybrid material. This *bonding* criterion divides hybrid materials into two distinct classes (6).

Class I hybrids, in which the organic and inorganic compounds are bound together by ionic or weak chemical interactions (ionic, van der Waals, hydrogen bonds), and Class II hybrids, in which the organic and inorganic components are linked by strong chemical bonds (covalent, coordination bonds).

In the following sections, we will analyze some of the major groups of hybrid materials according to their chemical nature. Mainly due to historical reasons some of these groups have been more extensively studied and constitute very large families on their own, while others are just beginning to be recognized as promising novel types of hybrid materials. Yet, in order to give a broad and general overview of the emerging field of hybrid materials, a "weighted" account of these families according to their sizes will be avoided and a general description of each will be given instead.

2.1. Hybrids Based on Siloxane Bonds. Hybrid materials based on silicon networks (both natural and synthetic) are probably the most widely studied. In this very broad category, we could make a first initial distinction between those materials based on silicates and those based on sol–gel materials such as polysiloxanes, polysilsesquioxanes, or even silica.

The intercalation of organic compounds in mineral silicates can be considered as the first antecedent of hybrid inorganic–organic materials. Initially, it was intercalation chemistry, like that of simple neutral organic molecules such as alcohols, ketones, aromatic hydrocarbons, or phenols in clays of the smectite type. But despite their fundamental interest these were labile intercalates more relevant to the field of catalysis than as materials in themselves. Yet, eventually this field led to the preparation of stable intercalation adducts such as those

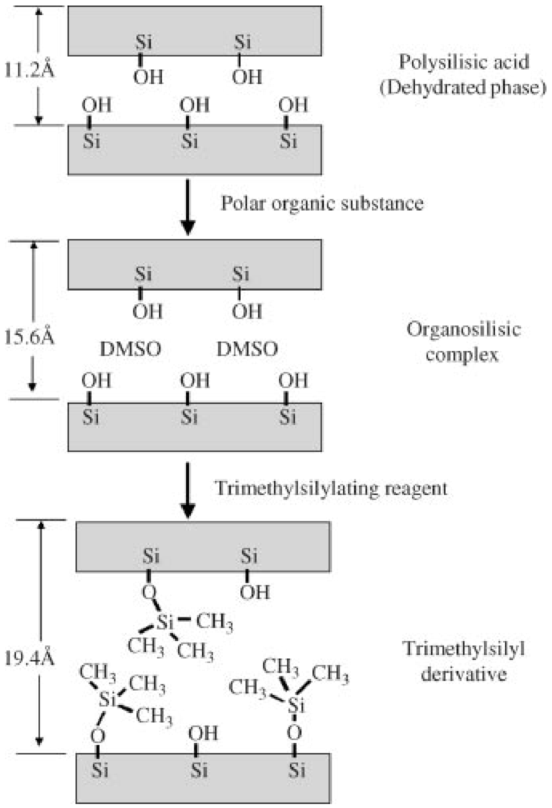
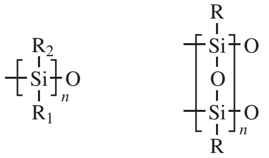


Fig. 3. Interlamellar grafting of trimethylsylil groups in a phyllosilicic acid mineral phase. From Ruiz-Hitzky and co-workers (5).

formed by intercalation of crown ethers into phyllosilicates (9) and later to the direct chemical modification of the interlamellar space in layered silicates (Fig. 3) by a process that came to be known as grafting (5,10); interestingly, a fitting term borrowed from the world of gardening that preceded the eventual blooming of hybrid materials.

The introduction of trimethylsylil groups in the example of Figure 3, is obviously just a first example leading the way to more complex organic derivatives resulting in novel hybrid inorganic–organic materials with characteristic structural and functional properties.



polysiloxane polysilsesquioxane

Fig. 4. Molecular formula of polysiloxane and polysilsesquioxane.

Table 1. **Glass-Transition Temperatures of Several Polysiloxanes (12)**

R_1	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	Phenyl
R_2	H	CH_3	Phenyl	CH_2CH_3	$(CH_2)_2CH_3$	$(CH_2)_2CF_3$	Phenyl
T_g(°C)	−138	−125	−90 to −75	−135	−120	−70	50 to 100

The development of hybrid materials based on the sol–gel growth of Si–O networks (6,11) opened the field by going beyond the limits imposed by the crystal chemistry of natural silicates, broadening substantially the kind of compounds which could be prepared. Among these sol–gel materials we can mention the single-chain polysiloxanes and the oxygen cross-linked polysilsesquioxanes, both of which could be formally considered to be condensation products in between molecular organosilanes (ie, SiR_4) and silica (SiO_2). Polysilsesquioxanes, with an extra oxygen bridge between silicon atoms represent the polymers closer to three-dimensional silica (see Fig. 4).

These polymers can be obtained by sol–gel condensation reactions similar to the process of preparation of SiO_2 gels. Thus, $R_1R_2Si(OR)_2$ and $R_1Si(OR)_3$ leading to polysiloxanes and polysilsesquioxanes in the same way that $Si(OR)_4$ leads to silica. Due precisely to their single flexible linear chain, polysiloxanes present low glass transition temperatures (Table 1), which can nevertheless be controlled by the use of adequate substituents.

On the other hand, the cross-linked nature of polysilsesquioxanes confers them higher glass transition temperatures in addition to higher thermal stability.

A further step in the control of molecular structure with these polymers comes from the introduction of bridged polysilsesquioxanes (13). By using adequate monomer units formed by an organic group with two or more—$Si(OR)_3$ moieties (Fig. 5) the connectivity between silicon atoms increases and the organic bridge can be used as a *spacer* that size and nature allow the controlled design of nanostructure as well as function (13–16).

2.2. POSS: A Case Study of Silicon-Based Commercial Hybrids. Polyhedral oligomeric silselsquioxanes (POSS) constitute an interesting example of Si–C hybrid materials already in the market and as such we have included

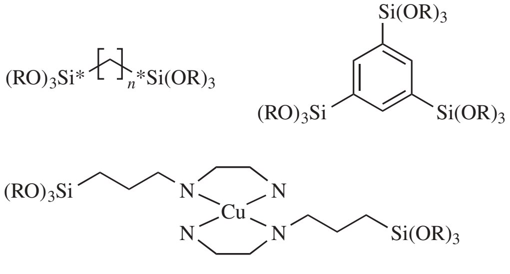
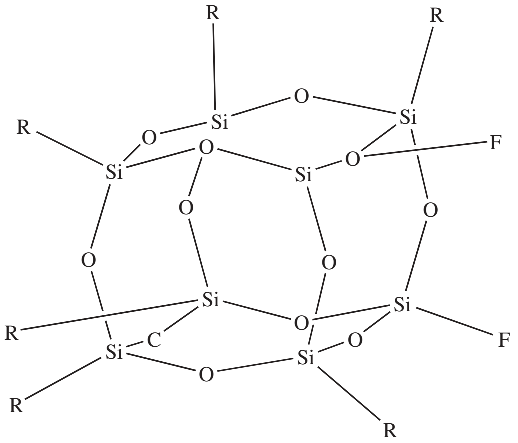


Fig. 5. Some of the possible building blocks for the design of bridged polysilsesquioxanes. (From Ref. 14).



Cubic silesquioxane $[RSiO_{1.5}]_8$

Fig. 6. Schematic representation of a CSS, the building blocks of POSS and one of the smallest possible units of ceramic silica.

here a description of their nature and properties. POSS are Si−O oligomeric clusters made of $R{-}SiO_3$ tetrahedra assembled into eight-cornered cages known as cubic silsesquioxanes (CSS). A representative example is given by the cluster $[RSiO_{1.5}]_8$, shown in Figure 6, which is one of the smallest possible units of ceramic silica. This Si-based cube in the nanometer size range (∼0.50 nm), has eight possible sites for functionalization (represented by R in Fig. 6) for the synthesis of hybrid organic−inorganic materials.

Several synthetic methods for the preparation of these hybrid materials have been described before (17) but can be grouped in three main types, namely, (*1*) *filler*, (*2*) *pedant*, and (*3*) *network* methods. In the first method, *filler*, the CSS is mechanically dispersed in the organic matrix, thus, no covalent linkage is observed. By contrast, the other two methods include the functionalization of the CSS (by the −R groups) and covalently linking them to the polymer. The difference between *pedant* and *network* methods is the number of functionalized linkages per CSS: one for the *pedant* and multiple for the *network* method. As it should be expected, each kind of synthesis leads to different hybrid properties. For example, the *pedant* method could be used to produce hybrids of organic polymers with bulky inorganic side groups (a thermoplastic material) whereas the *network* method would result in a three-dimensionally cross-linked hybrid material (a thermoset material) (17).

The use of POSS for the design and synthesis of new hybrid materials is in continuous growth. The possibility of attaching of different organic functional groups to their structure, together with their commercial availability makes this materials very useful for immediate new applications. We can find many hybrid organic−inorganic materials based on POSS and organic polymers (18), or as liquid crystalline hybrid materials (18−20), etc.

To finish our brief discussion of silicon-based hybrids, we should mention that their development is far from being exhausted. New and exciting approaches for the design of functional materials (4) based on this type of hybrids are on their way following several approaches that include the understanding and control of biomineralization (21) or the use of preformed nanobuilding blocks (22,23). Even in this latter specific approach several lines of work are possible and have been tried: the use of well-known molecular clusters (24) or the use of nanoparticles as building blocks (25).

2.3. Hybrids Based on Transition Metal Oxides.

In addition to silicate minerals, transition-metal oxides constitute the other large category of inorganic solids extensively studied as intercalation hosts and later used for the development of hybrid inorganic–organic materials.

As for silicates, intercalation chemistry in layered metal oxides was a first fundamental step to understand organic–inorganic interactions although initially the greatest driving force for these studies stemmed from their relevance in catalysis.

Layered oxides of the early transition elements such as V_2O_5 or MoO_3 were among the earliest and most widely studied in relation to their ability to insert small organic molecules first (26) and organic polymeric materials later (27) in between the inorganic slabs. The interest of these early hybrid materials was centered on the change in transport properties taking place in going from the inorganic oxides to the hybrid derivatives incorporating either ionically conducting polymers, such as poly(ethylene oxide) (PEO) or electronically conducting polymers such as polyaniline (PAni). These materials also offered an opportunity to grow those conducting polymers in a constrained anisotropic environment, thus avoiding chain interactions as found in the bulk polymers. Thus, most of the initial work in the field had a basic, rather than applied interest.

On the other hand, the use of oxides and conducting polymers for the design of hybrid materials allowed for a change in emphasis from structural to functional materials. Whereas the main strength of silicon networks was the control of structure and microstructure, the variety of chemical, magnetic, or electronic properties in transition-metal oxides offered wider opportunities to prepare functional hybrids. Furthermore, not only the inorganic oxides, but also the organic materials inserted into them, namely ionically or electronically conducting polymers, could contribute with their own activity and allow for the design of multifunctional materials (4).

In this respect, we can mention the first example of intercalation of the well-known ion-conducting polymer PEO into a solid, the layered silicate montmorillonite (27,28).

Concerning hybrids based on intrinsically conducting polymers, some of the systems studied in more detail comprise early transition metal oxides such as V_2O_5 and MoO_3 and conducting polymers (normally polyaniline, polypyrrole or polythiophene derivatives) (28–43). These systems have been the subject of basic chemical and structural studies, as well as efforts to determine their possible application as lithium-inserting cathodes in rechargeable lithium batteries. Concerning the former, the hybrid PAni/V_2O_5 has been extensively studied and the insertion of polymer chains in the interlayer space of the oxide (displacing water) has been demonstrated (44). Furthermore, the possibility to insert a single or a double layer of polyaniline depending on the synthetic conditions has been shown (32).

From a functional point of view, the combined electroactivity of these materials has been targeted for their use as electrodes in lithium batteries, (31,34) but their interest reaches other fields. For example, a hybrid such as Pani/V_2O_5 is formed with a mutual and concomitant doping process in which the inorganic oxide is n-doped while the organic polymer is p-doped, offering an interesting system for more fundamental studies.

2.4. Hybrids Based on Other Mineral Solids. When it comes to layered inorganic phases, oxides are just part of a wider family of inorganic mineral compounds with interlayer spacing suitable for insertion of organic compounds and polymers. Thus, the group of I–O hybrids includes materials based on a wide variety of inorganic hosts.

At this point, note that a true host–guest association would imply that the organic molecule could leave the inorganic structure reversibly, which is normally not the case for the hybrid materials described here. Indeed, the key to the preparation of many of these I–O hybrid materials rely upon in situ polymerization of the corresponding monomers once intercalated into the inorganic host or alternatively on the simultaneous formation of both organic and inorganic polymeric structures. Otherwise, the long chains and large molecular weights of the frequently insoluble polymers inserted would prevent their effective diffusion into the host structure. As a matter of fact, the irreversible character of the insertion process leading to the permanent integration of the organic and inorganic components is normally an important condition in the design of hybrid materials.

Examples of this type of I–O hybrid materials include insertion compounds of conducting organic polymers (COPs) in layered oxides like MoS_2 (45–47), chlorides like $RuCl_3$ (48), and oxychlorides like FeOCl (49–57), silicates and phosphates (58) (α-$VOPO_4$ (59,60), UO_2PO_4 (61), $CdPS_3$ and $NiPS_3$ (62), as well as the insertion within the channels of zeolitic solids (58,63–69). A related large group of hybrids formed by COPs and inorganic polymers of the Prussian blue family ($Fe[Fe(CN)_6]$) (70–76) can also be considered within this category, although in that case the structure of the hybrid and its intercalate nature are less well established.

2.5. Hybrids Based on Organic Polymers. To finish our discussion on the chemical aspects of hybrid materials, we will consider the category of organic–Inorganic hybrids. Normally, these are materials with organic polymers forming the predominant or host matrix where a variety of inorganic species can be embedded.

Within this category of O–I hybrid materials we could distinguish two types according to the polymers used, one where *conventional* (insulating) polymers provide the structural base, and another one with *conducting* polymers (electronic or ionic) contributing their peculiar combination of semiconducting and electrochemical behavior to the development of functional materials.

Concerning materials based on *conventional*, insulating organic polymers, the field has evolved from the simple use of inorganic additives and fillers in order to get mixtures with certain improved properties to the design of true hybrid materials with organic and inorganic components interacting at the molecular level.

An interesting example in this respect is the development of methods to produce exfoliated nanocomposites from in situ polymerization within layered silicates. As we discussed above, those same layered silicates intercalated with organic polymers constitute a classical example of inorganic–organic (I–O) hybrids. This exfoliated systems represent the ultimate level of dispersion between extended solids and polymers and constitute organic–inorganic (O–I) systems with single inorganic layers dispersed within a polymer matrix.

Another example of inorganic species within conventional organic polymers are a series of star polymers with inorganic cores based on polystyrene–W_6S_8 nanocomposites (77,78). As a totally different example we can mentioned a hybrid based on electrically conducting polymer, polyaniline, and TiO_2. This hybrid material is used to improve photoconducting properties on optoelectronic-based applications (79–85) or solar cells (84). In these materials, TiO_2 can be present as a thin layer on conducting organic polymer film (79) or it can be used as a true mixture of 80% TiO_2 in the conducting polymer (81,86). In the first case, we could talk about the formation of a hybrid heterostructure, where the organic–inorganic interaction is critical to properties and applications but without the molecular level dispersion found in nanocomposites like the latter example.

In addition to these examples of fundamental interest, hybrid materials based on conventional polymers are also making it to the market. We can already find examples of commercial success. Polyethylene, used for insulation of electrical wires, presents excellent mechanical and processing properties. Yet, to meet the ever-growing demands in performance, the material has been engineered to stand higher temperatures. This has been accomplished by modification with pendant alkoxysilanes that cross-link by a hydrolytic mechanism to form silsesquioxane networks. The resulting material can also be used as heat-shrinkable tubing and compression-resistant foams (87).

Other practical example of a hybrid organic–inorganic composite material is the use of polyvinyl alcohol and/or polypropylene fibers in high-performance concrete (HPC). The properties of the concrete can be modify by reducing the size and amount of crack source at different scales. The hybrid fibers combined with expansive agent provide better enhancement for shrinkage resistance and impermeability of HPC than the typical method of incorporation of hybrid fibers or expansive agent (88).

Other examples of polymer-based hybrid organic–inorganic materials are poly(vinyl alcohol)–$CuSO_4$ (89); polyimine–heteropolyanions (90); poly(methyl methacrylate)–BiI_3 (89); poly(acrylamide)–$TbCl_3$ (91); polyacrylamide–$H_3PMo_{12}O_{40}$ (92,93); nylon 6–$FeCl_3$ (89); poly(acrylamide)–$BiCl_3$ (89,94).

Many of the organic–inorganic hybrid materials based on *insulating* polymers, like the ones described above, present remarkable properties such as flexibility, mechanical strength, optical density, thermal and mechanical properties, etc, that makes them appropriate as structural, biomedical or electrical and thermal insulating materials. For other applications where good electronic or ionic transport properties are required, these hybrids are no longer useful. In those cases, organic–inorganic hybrid materials based on *conducting* polymers come to add the conductivity and functionality of those remarkable polymers towards the design of functional materials.

Within materials based on *conducting* polymers, we can distinguish those based on ion-conducting polymers (with poly(ethylene oxide) or PEO as a typical example) and those based on electronic conducting polymers (either electron or hole conductors, such as polyaniline, polypyrrole, polythiofene, etc). The latter can be used for their intrinsic conducting properties but also for their reversible electroactivity and mixed ion–electron conductivity.

Related to ionic conducting polymers the best example could be the use of PEO with different inorganic species, reviewed in reference (28). PEO was first intercalated into the layered silicate montmorillonite (27,44), and later in graphite (95), and has been used to form composite mixtures with SiO_2 and phosphotungstic acid for membranes (96,97), other related polymers such as polypropylene oxide and polytetramethylene oxide have also been used for this purpose (98), intercalated into different layered solids such as phyllosilicates (smectites) (99–101), vanadium pentoxide xerogel (102), or even transition metal chalcogenides (28). This polymer shows an excellent ionic conductivity making it a good choice as electrolyte for Li batteries (103). Other examples of PEO hybrid marterials are PEO–WCl_6 (89,104); PEO–$SnCl_4$ (89,104); PEO– $RbAg_4I_5$ (105); PEO – SiO_2 (106). But other ionic polymers are also on the list of organic inorganic hybrid materials, this is the case of PBI with common inorganic acids (107) or active acids from polyoxometalates (108).

The area of lithium batteries has received much attention in order to develop solid electrolytes with improved conductivity (109). Recent research efforts have shown an improvement in ionic conductivity by application of novel hybrid organic–inorganic polyelectrolytes. Di Noto and co-workers (110) and Popall and co-worker (111) classified hybrid organic–inorganic solid polymer electrolytes according to four different types: (*1*) Classical electrolytes based on organic macromolecules (polyelectrolytes PEO, polyethylene imine, polysulfides, polyethylene glycol, etc.) doped with inorganic salts (112–115); (*2*) nanocomposite polymer electrolytes that are inorganic oxides (ceramics) in contact with polymeric chains (116); (*3*) class 1 electrolytes based on organic macromolecules with metal and non-metal alkoxides (ORMOCERS) (ORMOCERS-APE–organically modified ceramics based on functionalized alkoxysilanes as polymer electrolytes) (111,117–120), and (*4*) class 2 electrolytes based on zeolitic inorganic–organic polymer electrolytes (Z-IOPE) (110,121).

The design of organic–inorganic hybrids based on *conducting* organic polymers provide another interesting way to introduce molecular inorganic species into conducting polymer networks, thus integrating the activity of those molecular species into useful extended materials. There are two major ways to accomplish this integration, the covalent linkage of molecules to form Class II hybrids or their incorporation as counterions to form Class I materials. In both cases, in addition to useful applications, fundamental questions arise such as electron transfer or ion transport within these complex molecular architectures. Some Recent Reviews Can be found in the literature on this topic (122–137).

The simplest way to obtain organic–inorganic hybrids with molecular species integrated in conducting polymers is taking advantage of counterion incorporation during the doping process of the polymers. Doping of these polymers involves the incorporation of charge-balancing species into the structure, anions for p-doped and cations for n-doped materials. Hence, the possibility of using active ionic species as dopants for the design of functional hybrids either by ionic exchange or by in situ incorporation of the active species during the polymerization and doping process. Examples of COPs that can be doped with anions species are polyaniline or polypyrrol; and polyacetylene is a good example of COP, which can be doped with cations.

This doping process leads to less strongly bound inorganic species (ie, class I hybrids) but has the advantage of a greater simplicity and versatility and has allowed the systematic preparation and study of hybrids containing a wide variety of anionic transition-metal complexes such as tetrachloroferrate (138–143), hexacyanoferrate (144–150), and other cyano-metalate complexes, (151,152), coordination compounds such as oxalatometalates, (153,154), or ethylenediaminetetraacetic acid, EDTA, complexes (155,156), tetrathiomolybdate (157–164), and macrocyclic compounds like metal phthalocyanine (156,165–175), or porphyrine (176,177) complexes. Among polynuclear metal complexes, polyoxometalates have been by far the most widely studied (4,147–149,178–181) different examples of these oxide clusters have been used to modify or get incorporated into polyacetylene, polypyrrole, poly(*N*-methylpyrrole), polyaniline, and polythiophenes (4).

2.6. Hybrid Materials Made of Conducting Organic Polymers Doped with Electroactive Molecular Clusters. A Case Study. The design of hybrid materials by doping of conducting polymers can be perfectly illustrated with the case of polyoxometalates. These are small oxide clusters traditionally considered within the framework of molecular chemistry (182,183). They are indeed complex molecules with several metallic ions coordinated by shared oxide ions, forming a highly symmetrical metal oxide cluster. Polyoxometalates can contain one or more kinds of atoms in addition to oxygen, respectively. These so-called addenda atoms are typically early transition metals such as W or Mo, and to a lesser extent V, Nb, or Ta. The minor components of heteropolyanions are known as heteroatoms and they can be anything, from main group elements to transition metals to lanthanides (182) conferring an extraordinary chemical richness to this large family of polynuclear compounds.

The concentration and distribution of active inorganic species in O–I hybrids can vary widely depending on the particular conditions of preparation. In principle, the amount of active anions incorporated to the hybrid is limited by the doping level attained for each particular polymer. But in addition, the presence of other (inactive) anions in the reaction or doping medium can decrease even further the amount of active species in the hybrid.

On the other hand, it must be stressed that different applications will impose different requirements on the design of a particular material, its form and composition. Thus, O–I hybrids used as supported catalysts might not require large bulk concentrations of active species but an increased concentration at the surface of the materials. Most of the earlier work conducted on polyoxometalate-doped COPs was aimed at the preparation of supported catalysts (4,184–188) and references therein. In those cases the concentration of polyoxometalates was secondary, counteranions like ClO_4^- from the acidic medium or HSO_4^- resulting from the reaction of aniline with persulfate would compete with polyoxometalate anions in the doping of the polymers. On other applications where the amount of active species is crucial, an optimal doping of the polymer must be sought to maximize the amount of anions incorporated, their distribution and the conductivity of the hybrid. Furthermore, in these cases care must be taken to avoid the presence of inactive anions that could compete for the doping of the polymers (4,35,178,189–196). This is the case for instance in the application of O–I hybrid materials for energy storage, where up to one molecule of phosphomolybdate anion ($[PMo_{12}O_{40}]^{3-}$) per nine aniline rings can be loaded into the corresponding hybrid (35,190) (compared with the maximum expected value of (1) $[PMo_{12}O_{40}]^{3-}$ per 6 aniline rings), whereas in the case of hexacyanoferrate hybrids prepared also in the absence of other anions, up to one $[Fe(CN)_6]^{3-}$ anion per 10 pyrrole rings was obtained (147–149,197) (close to the optimal expected value of 1 molecule per 9 pyrrole rings).

The retention of large active anions in these hybrid materials has important consequences regarding their redox insertion mechanism. The permanence of the anions in the polymer matrix upon reduction forces the insertion of cations for the needed charge balance, with the inverse process of cation expulsion taking place upon reoxidation, thus converting p-doped polymers into cation-inserting redox materials (191). The possibility of converting p-doped COPs into cation-inserting polymers opens new possibilities for their application, eg, as selective membranes or sensors, or for their integration in energy storage devices (4).

Whereas bulky molecular clusters of the polyoxometalate type are easily anchored within COPs the question remains as to whether smaller active anions would also be. The electroactive hexacyanoferrate anion $[Fe(CN)_6]^{3-/4-}$ (HCF) and its hybrid with PPy provide an interesting example in this respect. Some experimental evidence suggested that the permanence or loss of HCF anions in PPy was potential dependent (181); furthermore, cation incorporation into PPy–HCF hybrids has been reported to take place only when just the reduction of the HCF anion was involved, whereas the electrochemical reduction of the polymer (all in aqueous KNO_3) led to the deinsertion of hexacyanoferrate ions (181,198). The nature of counterionic cations also plays a role in the redox behavior of HCF doped into PPy. All these factors, which seem to complicate the redox chemistry and insertion/deinsertion properties of these hybrid materials can nevertheless be turned into useful behavior. Thus, films of PPy–HCF hybrids were used to demonstrate the feasibility of switching between a strongly bound state for HCF in the polymer to the release of controlled amounts of the anion by cathodic current pulses in what could be considered a model for drug-release chemical systems (198).

The electrolyte solvent is another important factor to take into account when considering the possible anchoring of HCF in conducting polymers. A study conducted on PPy materials showed that diffusion coefficients of anions in PPy [I^-, Cl^- and $Fe(CN)_6^{4-}$ were studied] are strongly dependent on the solvent due to the different solvation and swelling of the polymer in each case (199). Concerning specifically the anchoring of HCF, it has been found that repeated redox cycling of PPy–HCF hybrids results in HCF deinsertion when aqueous electrolytes are used, whereas the use of certain organic solvents for the electrolyte allow for the retention of the anion and consequent insertion of cations for balancing the charge during the reduction process. This feature has allowed the use of PPy–HCF and also PAni–HCF (146,148,149,179) as active cathode materials in reversible lithium cells, where non–aqueous solvents are commonly used.

In the above case-study, we analyzed in some detail how to take advantage of the doping process in COPs in order to anchor large or even medium-sized active anions into their networks. But in principle the “active-anion" doping approach seems obviously limited to anionic molecules when dealing with the most common p-doped COPs. However, there are several ways to overcome this expected limitation. A suitable substitution of neutral ligands with anionic functional groups, eg, can turn neutral or even cationic complexes into anions. Thus, sulfonated ligands were used, eg, for the integration of the metal phthalocyanine complexes mentioned above or iron trisphenantroline sulphonic acid complexes (200) into COPs. In addition to the doping species, the polymers themselves can also be derivatized by sulfonation (201) or substitution with other anionic groups such as alkylcarboxylic acids (202). This sometimes called self-doping approach leads as well to cation-inserting materials. In the above examples, applications were aimed to the manufacture of cathodes for lithium batteries (201) and proton-pump electrodes (202), respectively. Another way to introduce cationic species into p-doped COPs is the previous doping of the COPs with anionic organic polyelectrolytes that—similarly to the inorganic polyoxometalets described above—have a hindered diffusion out of the matrix (180,200). On the other hand, the interaction between *two* organic polymers or organic compounds give a special kind of hybrid material that we call here organic–organic hybrid (O–O). One interesting system of this kind is the one made of PEDOT and PSS$^+$ (203,204). In this case, the molecular composite material formed by two organic compounds yields a hybrid with improved characteristics to be used in photovoltaic devices. The material is already a commercial product under the name of BAYTRON.

3. Structural Aspects and Types

Most hybrids based on polymers, organic or inorganic, tend to be amorphous or, at most, poorly crystaline. Thus, polysiloxanes or polisilsesquioxanes, as well as organic polymer hybrids show no long-range order. Yet, there is another type of hybrids, namely, those based on mineral inorganic compounds where the structure of the crystalline phase is preserved in their hybrid materials, at least in principle, as well as other synthetic crystalline hybrid materials such as those based on mesoporous silica. We will discuss here structural aspects of these materials that range from crystal structure characterization to nanostructure and mesoporous architectures.

3.1. Crystalline Materials.

Among crystalline hybrid compounds we can distinguish layered and three-dimensional crystal structures.

Layered and Intercalate Hybrids. Among crystalline hybrids, those based on layered structures are probably the most common. Hybrids based on layered silicates (101,205–210), oxides (7,97,211–214), as well as sulfides (215,216) and other chalcogenides (217) have been extensively studied. Their structural changes upon insertion of organic components within the layers are well understood and normally correspond to an expansion of the inter–layer spacing.

Yet, even within a single hybrid system one can find certain structural variety. A good example is provided by the insertion of conducting polymers such as polyaniline within the slabs of V_2O_5 xerogels. These PAni/V_2O_5 hybrid materials can be formed by diffusion of aniline monomers into the inorganic network followed by their polymerization, or else, by simultaneous formation of the organic and inorganic networks. The crystal structure and the degree of order of these materials can be followed by means of powder X-ray diffraction. Figure 7

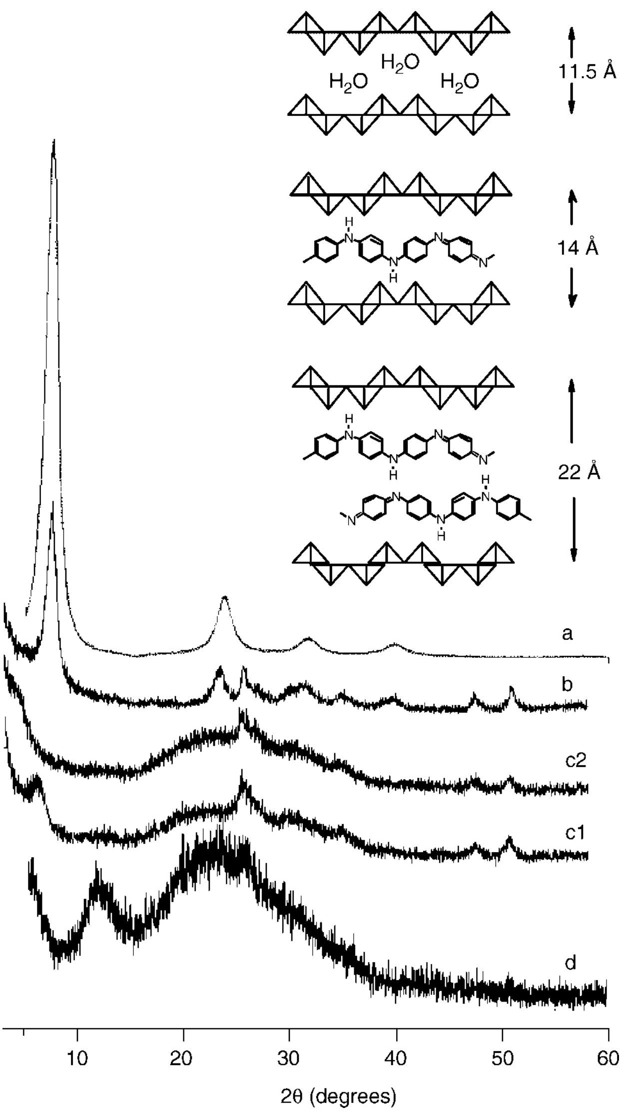


Fig. 7. X-ray diffraction patterns for V_2O_5 and related hybrid materials. (**a**) Oriented films of V_2O_5 showing preferential orientation (enhanced intensity for *00l* peaks). (**b**) V_2O_5 xerogel powder. (**c1**). PAni-V_2O_5 hybrid with a monolayer of PAni inserted in the oxide (001 peak indicates a spacing of 14 Å). (**c2**) PAni-V_2O_5 hybrid with a double layer of PAni inserted in the oxide (001 peak indicates a spacing of 22 Å). (**d**) PAni-V_2O_5 hybrid prepared for an extended period of 194 h (as compared with one hour for samples **c1** and **c2**). From Refs. (4,32).

shows powder diffraction patterns for V_2O_5 grown as oriented films (*1*) and as homogeneous powder (*2*), as well as for several PAni/V_2O_5 hybrids (**c1**,**c2**,**d**). For V_2O_5 it is already evident the effect of material growing conditions on order and structure. The presence of preferential orientation in films (*1*) is evidenced by the increased intensity of *00l* diffraction peaks (especially *001*) as compared with powder samples (*2*). The corresponding hybrid materials maintain these structural differences. The insertion of conducting polymers (PAni in the case of these data) within V_2O_5 leads to an expansion of the interlayer spacing. The shift of the intense 001 peak in the X-ray diffraction pattern (Fig. 7**c**1) indicates a change in the *c* axis from 11.5 Å for V_2O_5 to ~14 Å for PAni/V_2O_5, which is consistent with the substitution of the xerogel water molecules for PAni chains. Furthermore, a systematic study of aniline-rich reaction mixtures has shown that it is possible to identify two intercalate phases among polycrystalline PAni/V_2O_5 hybrids, corresponding to a single and a double layer of PAni inserted in the interlayer space (32). Traces **c1** and **c2** in Figure 7 correspond to these single and double intercalates that show spacings of ~14 and 22 Å, respectively. The inset figure shows schematic drawings and spacings corresponding to these materials and the hydrated xerogel.

In addition to the expansion of the unit cell, insertion of polyaniline into V_2O_5 results in loss of crystallinity as shown by the broader, less intense 001 peak , as well as by the broad diffuse scattering feature centered at ~25° in 2 theta. Indeed, for long reaction times, the diffraction patterns of aged materials shift from truly IO hybrids with a V_2O_5 dominated structure to materials in which the structure of the organic chains seems to take over (4). This is shown by the final loss of crystallinity evidenced in Figure 7**d**, an X-ray diffraction pattern where peaks characteristic of V_2O_5 have disappeared and only diffuse scattering features from the polymer are left. This final material could therefore be considered a borderline case between I–O and O–I hybrids and could be rightfully labeled as a hybrid polymeric material.

3.2. Three-dimensional Architectures: Mesostructured Hybrid Materials.

Zeolite minerals provide a good example of three-dimensional channeled networks in which a huge variety of organic substrates have been intercalated and studied. As for transition metal oxides, the insertion of organic substrates into zeolites initially had (and still has) interest from the point of view of catalysis. Also similarly to what was described for layered oxide phases, true hybrid materials have been subsequently made by insertion of polymers in natural and synthetic zeolites. Conducting polymers have also been inserted within the channels of zeolites providing a restrained environment for the ordered growth of single-chain polyaniline molecules akin to molecular wires (63,65,66,68,218).

But in the field of hybrid materials there has been a tremendous step forward in going beyond the molecular and crystal-structure domain to reach the development of mesostructured architectures.

The design of hybrid materials with porosity or structure in between the microscopic crystal structure and the macroscopic dimension deserves some comment here to finish our discussion on structural aspects of hybrid materials.

Mesoporous solids both organic and inorganic were developed separately, but following nature's own approach (see the section on hybrid biomaterials below), many research groups discovered the advantages of combining dissimilar components to form organic–inorganic hybrids in which self-organization arouse at the mesoscopic level (219). These approach similar to natural biomineralization has led to a wealth of literature on siliceous (220) as well as non-siliceous (Al, Ti, Zr, etc) (221) hybrid mesoporous materials.

Initially, this approach was used for the formation of purely inorganic mesoporous materials by removal of the organic structure-forming templates, as initially obtained by researchers of Mobil Corporation back in 1992 (222,223). But true hybrid materials have also been produced. For example, taking advantage of preformed mesoporous MCMs (Mobil Crystalline Materials) (222,223), all sorts of organic components have been inserted, from phthalocyanines (224) to conducting organic polymers (63,65–68), for the application of membranes (224,225), as catalyst, or production of molecular wires (64,226), etc.

4. Properties and Applications

The fields of application of hybrid materials are as varied as the materials themselves, but in general we could distinguish two main avenues concerning the type of application for which they are targeted. A first one puts the main emphasis on the mechanical properties of the hybrids for their application as structural materials whereas a second one aims at the development of functional materials, where mechanical properties are secondary and chemical activity, physical properties or a combination of both are paramount.

4.1. Structural Hybrid Materials.

Mechanical, structural, or thermal properties of materials can be improved by the use of hybrid organic–inorganic materials. We have already mentioned some examples such as the application of hybrid polymers as wire and cable insulation. Indeed, hybrid materials are already in the market, at least in the field of structural applications.

A remarkable example is that of POSS nanometric inorganic units that are embedded into polymer matrices to form nanostructured hybrid materials. Incorporation of POSS into traditional plastics results in polymeric nanocomposites that show many advantages relative to traditional plastics, such as an increased heat resistance and hardness, as well as decreased flammability and heat evolution. POSS technology has numerous applications in biological systems, pharmaceuticals, electronics, medical plastics, consumer products, and in construction and transportation markets.

POSS are not an exception. When it comes to structural applications, hybrid materials normally rely upon silicon-based inorganic compounds (silsesquioxanes, silica, or silicates) and organic polymers. Some examples are the application of silsesquioxane hybrids as low-dielectric matrices for interconnection material in integrated circuits (227), or the application of SiO_2 dispersed in organic polymers for hard (228) or powder (229) coatings. As structural materials silicon-based hybrids have been used for their transparency in optical applications (230) or in gradient refractive (231) index lenses. Applications are extensive in the area of thin films and coatings, for example in coatings to avoid abrasion or as decoration like in the case of colored glasses (232), corrosion prevention, coatings for electrical components, scratch-resistant coatings for the automobile industry, as adhesives, in cosmetics, as impact modifiers, water repellant or cable insulating materials (87).

But in addition to present commercial applications, the field of hybrid materials promises great new breakthroughs. A remarkable example is the design of "intelligent" hybrid materials that can adapt to a certain environment or modify in-situ their properties according to the requirements of a particular application. To illustrate this concept, we can mention the self-passivating/self-healing behavior of a hybrid nanocomposite made of Nylon 6 and a layered silicate (PLSN) that after 10 min of oxygen plasma exposure forms a tough ceramic passivation layer on the polymer surface. This behavior makes the hybrid much more durable than Nylon 6 itself and has lead to considering the application of this material in harsh environments such as solid rocket motor exhaust (233). We can also find examples of this self-adapting behavior in protective coating applications based on conducting organic polymers, specifically polyaniline (PAni). When polyaniline is used as passivation coating on steel the polymer oxidizes iron metal to Fe^{2+} and in return PAni is reduced to its hydrogenated form (leucoemeraldine). In the presence of water and oxygen, the Fe^{2+} is oxidized to Fe^{3+} (as Fe_2O_3) and the polymer is reoxidized to its emeraldine base form (234).

Other applications of hybrid organic–inorganic materials related to property modulations is their application in electrorheology (ER). Typically, ER fluids are suspensions composed of micrometer size particles and dielectric liquids (235). An external electric field is applied to change the hybrid properties such as viscosity, yield stress, shear modulus, which affect flow properties. Those changes are caused by the formation of an internal chain-like structure due to the arrangement of the dispersed particles within the fluid. The chains are held together by interparticle forces, which have sufficient strength to inhibit fluid flow. When the electric field is removed, the particles return to their original random distribution. These properties fulfill the requirements that make ER fluids one of the most important actuators used in smart materials and structures. They are very promising materials for application as active engine mounts, shock absorbers, adaptive structures (236), fluid drive control, automobile vibration control or robotic systems (235). Conventional ER fluids can be composed of carbonaceous particles or zeolites. Some examples of hybrid materials used as ER fluids are colloidal hybrids of surfactant-modified polysaccharide and titanium oxide (237), polyaniline and melamine–formaldehyde resins (236), or silica-phenolic polymer (lithium salt) particles dispersed in silicone oil (235).

4.2. Functional Hybrid Materials. Structural hybrid materials have benefited from a head start in reaching commercial applications, but their functional counterparts are quickly catching up and constitute a very promising emerging field with even broader potential applications.

In a strict sense, functional materials are those with chemical, electrochemical, or photochemical activity, although a wider definition, would also include magnetic, electronic, and optical materials. Although we endorse this wider criterion, we will discuss separately the applications of functional hybrid materials with chemical or physical activities.

4.3. Functional Materials Based on Chemical Activity. A growing number of the hybrids described in the literature are based on chemically or electrochemically active components. As a matter of fact, both the organic and the inorganic components can be active in these functional hybrids. For example, electroactive inorganic compounds can be used for the development of hybrid electrodes in combination with conducting organic polymers, but the latter in turn are also electroactive. This electroactivity is behind the development of hybrid materials for electrocatalysis (122,238) or energy storage (35) applications where the electrochemical activity is paramount. Electrocatalytic reactions studied with hybrid electrodes range from the reduction of O_2 (172,239) and protons (240,241) or the oxidation of H_2 (242), oxidation (127,176), or hydrogenation (124) of organic substrates or inorganic oxoanions (243) electrocatalytic reduction of CO_2 (75) or environmental pollution abatement by electroreduction of Cr(VI) (244). On the other hand, concerning energy-storage applications, materials for supercapacitors (245) as well as for insertion electrodes in rechargeable lithium batteries (32,246,247) have been developed.

Examples of other applications include the harnessing of electrochromic, (136,180,248,249) and photoelectrochromic (85) properties, application in display devices (85), photovoltaics (80), and novel energy-conversion systems (83), proton-pump electrodes (202), sensors (250), or chemiresistive detectors that work as artificial “noses” and already outperform human olfaction in detecting for example biogenic amines (251).

Sensors are indeed one whole field with many interesting developments related to hybrid materials. Sol-gel techniques are getting a growing relevance in the manufacture of sensor structures (252). Incorporation, encapsulation or entrapment of organic or biological species is possible with materials synthesized by this method, thanks in part to their formation at room temperature. These strategies provide sturdy materials carrying active molecules capable of responding to chemical changes in the environment. The simplicity of this sol–gel approach has made of it the method of choice for routine fabrication of optical sensors. An example is the entrapment of different dyes within the same sol–gel host matrix to produce a multianalyte detection system (24).

Among hybrid organic–inorganic materials, we can find many other applications as sensors, including some dealing with new breakthroughs in miniaturization (253–256). A recent review about hybrid materials for sensors by Walcarius (257) describes sensors based on hybrids made of silica and organic molecules and their application in the field of electroanalytical chemistry. Active materials used for this purpose are dispersed in carbon pastes and include metal phthalocyanines such as FeTsPc, NiTsPc , Ru(edta)/ZrO_2 or methylene blue with titanium phosphate, cobalt porpyhyrin/titanium phosphate, and many others; all of them as part of silica-based organic–inorganic hybrid materials (257).

Sensors to analyze the aroma of virgin olive oil have been made out of conducting organic polymers, polypyrrole, and tetrasulfonated nickel phtalocyanine (NiPcTs) (258,259). Other examples include the application of sensors for the discrimination of odors for trim plastic materials used in automobiles. The sensors were based on conducting organic polymers and potassium ferrocyanide, $K_4Fe(CN)_6$ (260).

4.4. Functional Materials Based on Physical Properties. Electronics and optoelectronics are possibly two of the areas that could benefit more from the properties of hybrid organic inorganic materials. Recent reviews on this particular area of application can be found in the literature. Hybrids based on self assembly of siliceous hybrids (261) and general mesoporous and mesostructured materials (262). We can also find electronic and optoelectronic applications of hybrids based on conducting organic polymers (86) or other non-siliceous materials (221) like perovskites with organic molecules (263).

4.5. Hybrid Biomaterials. The fast-growing category of biomaterials obviously includes both structural and functional members, as we will see below. Yet, their very specific focus on biomedical applications have made us consider a separate section for these special materials.

Nature provides us with many examples of living species able to produce structural materials with remarkable mechanical properties, like wood, bone, seashells, or teeth. Some of these materials are also perfect examples of natural hybrid organic inorganic materials. Bone, eg, is a hybrid made of a matrix of structural protein fibrils of collagen and water-swollen anionic polysaccharides, reinforced with nanosized thin plates of hydroxyapatite (264). The system apatite–gelatine can be seen as a simplified model for teeth formation. Teeth are known to be the hardest calcium–phosphate based biomineral. Their high mechanical stability arises from their hierarchical structure of a complex organization of minute apatite crystals together with protein molecules (265).

The remarkable mechanical characteristics of structural hybrid biomaterials like teeth or bone, such as their high specific strength and modulus and high toughness, make them suitable models for *biomimetic* synthesis. This type of synthesis tries to imitate the building mechanics of biological systems to obtain composites that are ordered from the nanometer to the microscopic length scale (265). A recent review by Busch and co-workers deals with the specific process of biomimetic synthesis of fluoroapatite–gelatine composites and includes detailed descriptions and studies of nature-emulating synthesis and the final properties of the materials obtained (265).

The synthesis of biomaterials can be made applying different techniques such as the sol–gel process, building blocks, self-assembly, etc, all of them as part of the biomimetic aproach. It should be remarked that all these techniques have been widely used by many different groups with great success for the synthesis of hybrid materials not always related to biological systems. Some examples are alkoxysilanes in polymers including Poly(vinyl cloride), poly(methylmetacrylate), polybenzoxazoles, poly(butyl metacrylate), poly(ethylene oxide), poly(tetramethylene oxide), polyether sulfone, poly(dimethyl siloxane), etc (264).

Some biohybrids have been formed with titania, zirconia, and alumina with aramides (aromatic polyamides), poly(tetramethylene oxide), epoxides, etc. Bone or seashell layered architectures have inspired the formation of materials with similar fracture resistance. Some examples are the use of mica or clay-type silicates and suitable mono- or multifunctional monomers, or a polymer solution. For example, montmorillonite clays and alkyl amonioum ion (266), or aramide-clay composites (264). Layered silicates have also been reported by Giannelis and co-workers (267) using different polymers and also aniline as the organic component.

On the other hand, self-assembly is not the end of the road. Nature still has lots of things to teach us. Features such as functional adaptability or self-healing ability, characteristic of biological systems, represent extremely efficient processes that show the way ahead (264).

Functionality is also a key feature in Nature and as such, functional biomaterials should be also expected to make growing contributions in the near future.

Present applications include bioencapsulation of active biological materials such as enzymes, antibodies, living microbial, plant and animal cells, DNA, etc within ceramic matrices. In these cases, the combination of delicate functional biostructures with inorganic *ceramics* is possible thanks to the fact that the inorganic framework is formed at room temperature by sol–gel techniques. In most cases the final applications of bioencapsulates are the syntheses of nanocomposites for sensors, catalysis or diagnostic (268).

Finally, we will mention an emerging area dealing with biomolecular electronics (BME) that will probably experience an important growth in the near future and a growing interface with the field of hybrid materials. Presently, it relies on the assembly of self-organized devices based on biomolecular materials. Biomolecules are proposed both by their activity and robustness as compared with other simpler organic molecules, and could lead to cheap and easy-to-fabricate devices with self-assembling and self-healing/repairing characteristics. A couple of remarkable examples making use of biomolecules as state of the art materials are the use of the metalloprotein azurin for the assembly of single-molecule devices (269), or the fabrication of interconnects with DNA molecules (270–272).

5. Conclusion

This work has tried to provide a very general overview of the area of hybrid materials, an area that is presently in constant growth. This growing trend is easily confirmed by the increasing number of research papers published each year on the topic. Our aim in writing this article was not to compile a comprehensive review of the work in this field but to give a taste of the technological potential of hybrid materials and their applications introducing the reader to the very varied lines of work in the field and providing a starting point for further reading, including many very recent reviews.

Hybrid materials are not newcomers to the materials science arena anymore. In the last two decades they have grown and consolidated both as structural and functional materials showing the benefits of combining components with dissimilar properties at the molecular level to form improved new materials with synergic properties. As we have shown above, examples abound of how industry can improve product quality and reduce costs by applying the hybrid approach to the development of new and improved materials and novel applications.

Among all kinds of hybrid materials revised on this article, it seems that siloxane-based materials are already closer to marketable applications as structural materials and are also being developed for a variety of functional applications. Yet, the remarkably varied examples of hybrids discussed in this article, including functional and multifunctional materials like conducting polymers, should be enough to convey the idea that many more exciting developments are on their way.

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