CHAPTER I

Hybrid Materials: A very old history from mother nature to man-made materials.

For the past five hundred million years, nature has produced materials with remarkable properties and features such as the beautifully carved structures found in radiolarians or diatoms (see the opposite figure). Another of nature’s remarkable features is its ability to combine at the nanoscale (bio) organic and inorganic components allowing the construction of smart natural materials that found a compromise between different properties or functions (mechanics, density, permeability, colour, hydrophobicity, etc.). Such a high level of integration associates several aspects: miniaturisation whose object is to accommodate a maximum of elementary functions in a small volume, hybridisation between inorganic and organic components optimizing complementary possibilities, functions and hierarchy. Current examples of natural organic–inorganic composites are crustacean carapaces or mollusc shells and bone or teeth tissues in vertebrates.

As far as man-made materials are concerned, the possibility to combine properties of organic and inorganic components for materials design and processing is a very old challenge that likely started since ages (Egyptian inks, green bodies of china ceramics, prehistoric frescos, etc.). However, the so-called hybrid organic–inorganic materials are not simply physical mixtures. They can be broadly defined as nanocomposites with organic and inorganic components, intimately mixed. Indeed, hybrids are either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components’ domains has a dimension ranging from some Å to several nanometers. It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but the role of the inner interfaces could be predominant. The nature of the interface has been used to grossly divide these materials into two distinct classes. In class I, organic and inorganic components are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure. In class II materials, the two phases are linked together through strong chemical bonds (covalent or iono-covalent bonds).

Maya blue is a beautiful example of a remarkable quite old man-made class I hybrid material whose conception was the fruit of an ancient serendipitous discovery. Ancient Maya fresco paintings are characterized by bright blue colors that had been miraculously preserved (see the opposite figure). That particular Maya blue pigment had withstood more than twelve centuries of a harsh jungle environment looking almost as fresh as when it was used in the 8th century. Maya blue is indeed a robust pigment, not only resisting biodegradation, but showing also unprecedented stability when exposed to acids, alkalis and organic solvents. Maya blue is a hybrid organic–inorganic material with molecules of the natural blue indigo encapsulated within the channels of a clay mineral known as palygorskite (theoretical formula: $\text{Si}_8\text{O}_{20}\text{Al}_2\text{Mg}_2\text{OH}_2\text{(H}_2\text{O})_4\text{.4H}_2\text{O}$ – see the figure below). It is a manmade material that combines the color of the organic pigment and the resistance of the inorganic host, a synergic material, with properties and performance well beyond those of a simple mixture of its components.

The palygorskite structure is built from the assembly of successive layers of $\text{Si}_2\text{O}_5$ tetrahedra (green) alternatively pointing up and down ($\text{Si}^{4+}$ can be substituted by $\text{Al}^{3+}$ or $\text{Fe}^{3+}$), linked by discontinuous layers of $\text{MgO}_6$ octahedra (pink) ($\text{Mg}^{2+}$ can be substituted by $\text{Al}^{3+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ or rarely by $\text{Li}^{+}$, $\text{Cr}^{3+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$). This arrangement generates micro-channels (6.4*3.7 Å) along the axial direction where water molecules (and further organic molecules) are trapped (blue).
Considering the industrial era, successful commercial hybrid organic–inorganic polymers have been part of manufacturing technology since the 1950s. Paints are a good link between Mayas and modern applications of hybrids. Indeed, some of the oldest and most famous organic–inorganic industrial representatives are certainly coming from the paint industries, where inorganic nano-pigments are suspended in organic mixtures (solvents, surfactants, etc.). While the name of “hybrid” materials was not evoked at that time, the wide increase of work on organic–inorganic structures was pursued with the development of the polymer industry. The concept of “hybrid organic–inorganic” nanocomposites exploded in the eighties with the expansion of soft inorganic chemistry processes. Indeed the mild synthetic conditions offered by the sol–gel process (metallo-organic precursors, organic solvents, low processing temperatures, processing versatility of the colloidal state) allow the mixing of inorganic and organic components at the nanometric scale. Since then, the study of so-called functional hybrid nanocomposites became a mushrooming field of investigation yielding innovative advanced materials with high added value. These materials being at the interface of organic and inorganic realms are highly versatile offering a wide range of possibilities to elaborate tailor-made materials in terms of processing and chemical and physical properties.

Today, this potential is becoming real and many hybrid materials are entering niche markets that should expand in the future because new and stricter requirements are now being set up to achieve greater harmony between the environment and human activities. New materials and systems produced by man must in future aim at higher levels of sophistication and miniaturisation, be recyclable and respect the environment, be reliable and consume less energy. Without any doubt, hybrid materials will soon generate smart membranes, new catalysts and sensors, new generation of photovoltaic and fuel cells, smart microelectronic, micro-optical and photonic components and systems, or intelligent therapeutic vectors that combine targeting, imaging, therapy and controlled release properties.

References: