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POLYMER BASED HYBRID MATERIALS FOR AEROSPACE APPLICATIONS

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Abstract: *Hybrid materials represent one of the most fascinating class of materials developed in recent years. The tremendous possibilities of combination of different properties in one material initiated extensive research on potential novel materials and high performance applications.*

The aviation and aerospace industry is an area of major interest in terms of new solutions and innovation. The spin-off effect for technology from the aerospace industry to other industrial sectors is particularly pronounced for materials technology which, in the wider sense including computer modelling, interfaces and surface science, is a key instrument to meet challenges. This paper is intended as an overview of the main issues concerning the design and structure-properties relationship of hybrid materials for aerospace applications.

Keywords: *hybrid materials, aerospace applications, design, structure-properties relationship*

1. INTRODUCTION

The aerospace industry created the image of an ideal airplane: it would be extremely light weight, have wings with variable geometry, run on renewable energy, and would make no noise. After its lifetime, all its parts would be reusable or recyclable. Although far from the present-day situation, this vision is a valuable set of guidelines for the research and industry. The vision is aligned with the customers' expectations: low operating costs, high productivity and availability, low environmental impact, and simple operation and maintenance.

Improvements of the structural part of the aircraft will contribute to meet these demands. Large expectation are therefore attributed to new hybrid and multifunctional materials and coatings, e.g. for multifunctional airframes with smart technologies capable of structural

health monitoring, structural adaptation and self healing [1].

During the recent decades, the penetration of advanced composite and hybrid materials in the aircraft industry was significant. The use of composites in aircraft have increased from 5-6% in the 1980s (A310, Boeing 767), 10-15% in the 1990s (A340, Boeing 777), to 23% in the new A380 and up to 52% in the planned A350 and Boeing 787. This development is the result of the steadily increasing performance, reliability and diversity of these materials.

Five main classes of challenges for composite and hybrid materials in aircrafts have been identified: performance, functionality, manufacturing, environment and knowledge. Performance challenges are, for example, resistance to high and low temperature cycling, compression resistance, damage tolerance and reduction of life cycle costs. Functionality challenges are structural

health monitoring, management of noise and electrical hazards, validation of bonds, integration of smart systems. As for manufacturing, challenges are recycling and re-use, fabrication of large complex parts and reduction of manufacturing costs. The environmental challenges are related to finding alternatives to petroleum feedstock, lowering the energy use in manufacturing and designing for repair, recycling and re-use of parts. Finally, there are considerable challenges related to in-depth knowledge of long-term ageing effects, prediction of materials properties and characterization, envisage specific applications.

One basic demand for the hybrid materials used in present-day aircrafts is the optimization of the design of complex composite structures and for this purpose new knowledge and new modelling tools are required (interface interactions models can lead to lighter structures with longer lifetime and higher reliability; damage models should increase the damage tolerance of structures; etc.).

Another problem is that most composite materials that are in use today are electric insulators, which creates risks for uncontrolled electrical charges and sparks. Design of electrically conductive hybrid materials for aerospace industry is an important development topic.

Other tasks: composite structures with better and more reliable performance under humid conditions at high temperature (hot-wet performance), demand for fibre composites with higher compressive strength [2], smart materials able to react to external or internal changes or even switchable systems [3].

2. POLYMER BASED HYBRID MATERIALS STRUCTURE DESIGN

2.1 Structural considerations. Basically, a hybrid material includes two moieties blended on the molecular scale; commonly, one of these compounds is inorganic and the other one organic. A more detailed definition takes into consideration the possible

interactions between the inorganic and organic species. Class I hybrid materials show weak interactions (such as van der Waals, hydrogen bonding or weak electrostatic interactions), while class II hybrid materials present strong (covalent, coordinative, ionic) interactions between the components. Due to the gradual change in the strength of interactions, there is a steady transition between classes of hybrid materials (Fig. 1).

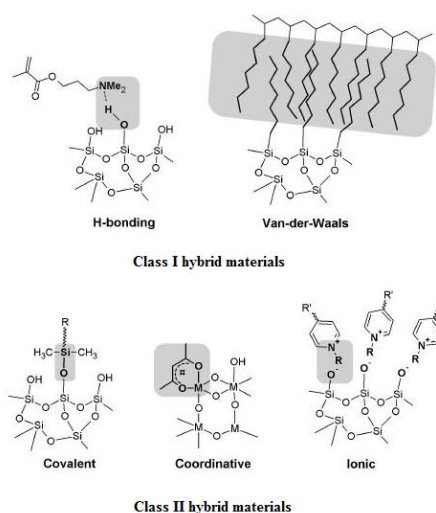


Fig. 1. Typical interactions in hybrid materials

Structural properties can also be used to distinguish between various hybrid materials. An organic moiety containing a functional group that allows the attachment to an inorganic network can act as a network modifier, builder or functionalizer [4].

Blends are formed if no strong chemical interactions exist between the inorganic and organic building blocks, e.g. an organic polymer with entrapped discrete inorganic moieties through physical interactions or the inorganic components are entrapped in a crosslinked polymer matrix. When an inorganic and an organic network interpenetrate each other, without strong chemical interactions, the so called interpenetrating networks (IPNs) are formed. Class II hybrids are yielding in the case of discrete inorganic building blocks, e.g. clusters, covalently bonded to the organic polymers or inorganic and organic polymers covalently connected with each other. A schematic presentation of these structures is shown in Fig. 2.



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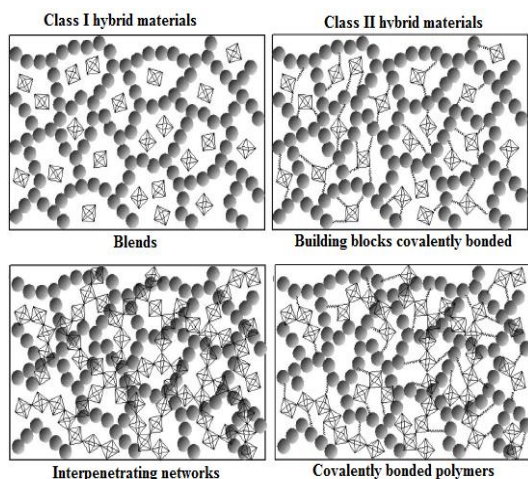


Fig. 2. Structural features of hybrid materials

2.2 Synthetic Strategies towards Hybrid Materials. Two different approaches can be used for obtaining hybrid materials:

- (A) well-defined preformed building blocks react with each other to form the final hybrid material in which the precursors maintain (at least, partially) their original integrity;
- (B) one or both structural units are formed from the precursors that are transformed into a novel (network) structure.

Both methodologies have their advantages and disadvantages.

Building block approach. Building blocks maintain (at least, partially) their molecular integrity throughout the material formation. At the same time, typical properties of these building blocks are transferred to the novel materials. Representative examples of such well-defined building blocks are modified inorganic clusters or nanoparticles with attached reactive organic groups (Fig. 3.). Cluster compounds often consist of at least one functional group that allows an interaction with an organic matrix. Two reactive groups can lead to the formation of chain structures, whilst building blocks having three reactive groups can be used for the formation of

crosslinked materials (without any additional molecules).

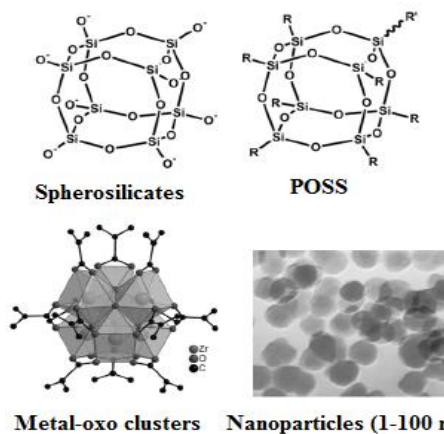


Fig. 3. Typical building blocks for hybrid materials

Beside the above mentioned molecular building blocks, nanosized building blocks, such as particles or nanorods, can also be used to form nanocomposites.

The building block approach has one large advantage compared with the *in situ* formation: because at least one structural unit is well-defined and usually does not undergo significant structural changes during the material formation, a better structure–property prediction is possible. Furthermore, the building blocks can be designed as to transfer their best performance in the new materials (i.e., good solubility of inorganic compounds in organic monomers by surface groups showing a similar polarity as the monomers).

***In situ* formation.** Contrary to the building block approach, the *in situ* formation of the hybrid materials is based on the chemical transformation of the precursors used for materials design and preparation. A typical example is the case when organic polymers are formed, but also the inorganic component is obtained by the sol–gel process. In these cases, well-defined discrete molecules are transformed into multidimensional structures,

which often show totally different properties from the original precursors. Simple, commercially available molecules are used and the internal structure of these hybrid materials is determined by the composition and reaction conditions. Therefore, control over the latter is a key step in this process. For example, if the inorganic species is a silica derivative formed by the sol-gel process, the change from base to acid catalysis yields in different structures: base catalysis leads to a particulate microstructure, while acid catalysis generates a polymer-like microstructure.

The sol-gel process. This process is chemically related to a polycondensation reaction. Usually, the reaction results in a three-dimensional crosslinked network. The fact that small molecules are used as precursors for the formation of the crosslinked materials implies several advantages: for example, a high control of the purity and composition of the final materials, the use of a solvent based chemistry which offers many advantages for the processing of the materials formed [5-7].

The silicon-based sol-gel process is probably the one that has been most investigated. The main feature of the silicon-based sol-gel processes is the incorporation of organic groups using organically modified silanes. Si-C bonds have enhanced stability against hydrolysis in the aqueous media, which is not the case for many metal-carbon bonds, so it is possible to incorporate a wide variety of organic groups in the formed network.

Principally, $R_{4-n}SiX_n$ compounds ($n = 1\div 4$, $X = OR'$, halogen) are used as molecular precursors, in which the Si-X bond is labile towards hydrolysis reactions, forming unstable silanols (Si-OH) that condensate yielding in Si-O-Si bonds. In the first steps of this reaction, oligo- and polymers, as well as cyclics, are formed subsequently resulting in colloids that define the sol. Solid particles in the sol undergo crosslinking reactions and form the gel. The process is catalyzed by acids or bases, resulting in different reaction mechanisms with distinct reaction rates and kinetics expressed by the gel point. In non-

hydrolytic sol-gel processes, the reaction between metal halides and alkoxides is used.

Formation of organic polymers in the presence of preformed inorganic components. In this specific case, there are several possibilities to overcome the incompatibility of the two species. The inorganic material surface can be modified with non-reactive organic groups (e.g., alkyl chains), or moieties that contain reactive surface groups (such as polymerizable functionalities). Depending on these, the material can be pretreated: for example, a pure inorganic surface can be treated with surfactants or silane coupling agents to make it compatible with the organic monomers, or functional monomers that react with the surface of the inorganic material can be added. If the inorganic component has nonreactive organic groups attached to its surface and it can be dissolved in a monomer which is subsequently polymerized, the resulting material is a blend. In this case, the inorganic component interact only weakly or not at all with the organic polymer; hence, a class I hybrid material is formed. Homogeneous materials are only obtained in this case if agglomeration of the inorganic components in the organic environment is prevented. This can be achieved if the interactions between the inorganic components and the monomers are better or at least the same as between the inorganic components. However, if no strong chemical interactions are formed, the long-term stability is questionable because of diffusion effects in the resulting hybrid material [8-10]. Examples of such materials are alkyl chain functionalized silica nanoparticles that can be introduced into many hydrophobic polymers, the use of block copolymers containing a poly(vinylpyridine) segment that can attach to many metal nanoparticles, or the use of hydroxyethyl methacrylates in the polymerization mixture together with metal oxide nanoparticles. The stronger the interaction between the components, the more stable is the final material, as in class II materials. Examples for such strong interactions are the surface-attached polymerizable groups that are copolymerized with organic monomers.



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If a porous 3D inorganic network is used as inorganic component, a different approach has to be employed depending on the pore size, the surface functionalization of the pores and the stiffness of the inorganic framework. In many cases, intercalation of organic components into the cavities is difficult because of diffusion limits. The 2D layered inorganic materials can intercalate organic molecules and, if polymerization between the layers occurs, even exfoliate, producing nanocomposites. The exfoliated hybrids only contain a small weight percentage of host layers with no structural order. Layered materials are able to completely delaminate if the forces produced by the intercalated polymers overcome the attracting energy of the single layers. This is not possible in the case of the stable 3D framework structures, such as zeolites, molecular sieves, etc.

Hybrid materials by simultaneous formation of both components. Simultaneous formation of the inorganic and organic polymers can result in the most homogeneous type of interpenetrating networks [3,11]. Usually, the precursors for the sol-gel process are mixed with monomers and both processes are carried out at the same time, with or without solvent. Applying this method, three processes are competing: (a) the kinetics of the hydrolysis and condensation forming the inorganic phase, (b) the kinetics of the polymerization of the organic phase, and (c) the thermodynamics of the phase separation. Tailoring the kinetics of the two polymerizations so they occur simultaneously and rapidly enough, phase separation can be avoided or minimized. Additional parameters, such as attractive interactions between moieties, can also be used to avoid phase separation.

One problem that also arises from the simultaneous formation of both networks is the

sensitivity of many polymerization processes or final materials towards sol-gel conditions. Ionic polymerization, for example, often interacts with the precursors or intermediates of the sol-gel process, so free radical polymerization is used instead.

An interesting route towards hybrid materials is the use of precursors that contain alkoxides which can also act as monomers in the organic polymerization. This leads to nanocomposites with reduced shrinkage and high homogeneity [3].

3. PROPERTIES AND APPLICATIONS

The new concept of "care-free structures" in aerospace industry [12] suggests that optimized structures should be designed for minimum cost-maximum performance and this approach is connected to the wide variety of possibilities offered by polymeric hybrid materials.

Environmental and safety concerns will drive the design of new aircrafts that will benefit from the hybrid materials. CNTs reinforces polymers are lightweight materials that will reduce the weight of aerospace crafts by 40%, hence the energy consumption, providing higher electrical and thermal conductivity. More than 4000 lb. (2 tons) of copper wire is used for commercial aircrafts (Boeing 747), replacing it with lighter CNTs hybrids will reduce the weight and enhance the performance. Same in the case of cryogenic propellant tanks of space crafts. Recent works has shown that the addition of organically modified clays to toughened epoxy resins leads to a 60% reduction in hydrogen permeability, enhanced compatibility with liquid oxygen and improved resistance to microcracking [13].

Polymer based composites and hybrid materials have high costs, but are excellent in damage tolerance and corrosion resistance which translates to low maintenance and high performance. For instance, the B787 with 50% composite is promising twice as long operation time between scheduled maintenance intervals of the B767 it replaces [14].

Laminates of aluminum and polymer composites provide exceptional fatigue-crack-growth resistance and damage tolerance at high specific strength. Hybrid laminates of titanium alloys, aluminum alloys and reinforced polymers are considered to provide combinations of properties beyond the capabilities of the current materials.

4. CONCLUSIONS

Towards new hybrid materials: modelling tools to optimise design, including damage and interface modelling; new polymers dedicated to hybrids (from renewable sources, recycled, "one-fits-all" polymers, reversible thermosets, self-healing polymers); new reinforcement materials (carbon and other fibres and other nano-carbon structures); multifunctional coatings (conductive, antifriction, self cleaning, de-icing/anti-icing, air cleaning, self-healing), smart materials.

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