Ph.D. COURSE IN INDUSTRIAL ENGINEERING – XXXI_ CYCLE

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Abstract of the thesis

Main objective of this PhD thesis is the development of a new generation of self-healing multifunctional composites able to overcome some of the current limitations of aeronautical materials, such as: absence of auto-repair mechanisms integrated in the composite structure, reduced electrical conductivity and poor impact damage resistance.

Structural aeronautical systems experience a broad spectrum of environmental and operational loads and atmospheric hazards (hail, lightning, storms etc.). Severe and/or prolonged load exposures may trigger the damage accumulation process even in recently deployed structures. Modern airframe design is exploiting new exciting developments in materials and structures to construct ever more efficient air vehicle able to enable 'smart' maintenance including self-repair capabilities. Relevant challenges for many of the already developed self-repairing systems are to enhance the structural stability, and the resistance to the atmospheric hazards through specific functions integrated in the material. The traditional approach to the development of aeronautic materials is to address the load-carrying and other functional requirements separately, resulting in a suboptimal load-bearing material with the penalty of added weight. The research activity of this PhD thesis is aimed to develop self-healing, load-bearing materials with all functionalities integrated in a single material able to meet many important requirements of this kind of materials. The main concept underpinning this PhD project is the use of the nanotechnology strategy for the production of new, high mechanical performance multifunctional materials. Based on recent developments in the field of nanotechnologies and successful strategies identified in recently papers and patents, the main objectives of this thesis have been achieved. The performed research activities allowed the implementation of a new generation of self-healing composites, which also considers relevant aspects related to the need of developing environmentally-friendly materials for transports.

In this project, many different approaches have been considered for each functionality in order to reduce the risk of failure. Alternative concepts with respect to designs already proposed in literature have been explored. Multifunctional resins prepared using chemicals not commercially available yet have been developed and characterized.

The research strategies for each functionality are summarized in the Table 1.

Table 1 *Research strategies related to the different functionality*

RESEARCH STRATEGIES	
Poor impact damage resistance Current limit: absence of auto-repair mechanisms in the composite structures	**Reduced electrical conductivity**
First approach Development of self-healing systems based on the microencapsulation concept	**First approach** Use of covalently functionalized electrically conductive carbon nanofillers embedded in the polymeric matrix
Second approach Development of supramolecular self-healing systems	**Second approach** Use of unfunctionalized electrically conductive carbon nanofillers embedded in a polymeric matrix suitable modified to host auto-repair mechanisms

RELEVANT RESULTS

- The approach based on the microencapsulation concept, has led to the synthesis of a new ruthenium catalyst, $HG2_{MesPhSyn}$, active in the Ring Opening Metathesis Polymerization (ROMP) of cyclic olefins and able to activate self-healing mechanisms in aeronautical structural resins. The new catalyst is characterized by high thermal stability and tolerance towards epoxy groups and aromatic primary amines (employed as curing agent for aeronautical resins).

- In the field of microencapsulated self-healing materials, a very relevant result related to the stereochemistry of the ROMP Catalyst $HG2_{MesPhSyn}$ has been found: the stereochemistry of the initiator has to be taken in high consideration before to formulate structural self-healing resins. It strongly affects the efficiency of the self-healing mechanisms.

- The approach based on the development of supramolecular self-healing systems, combined to the use of unfunctionalized or functionalized multiwall carbon nanotubes (MWCNTs), has allowed to design self-healing materials able to contrast the electrically insulating properties of aeronautical resins. To achieve this goal, the rigidity of the matrix has been reduced implementing a rubber material to modify the phase composition. It was demonstrated that the higher mobility of this rubber phase finely distributed in the composite, is most likely responsible for favouring the arrangement of hydrogen bonding interactions to activate self-healing mechanisms.

- Results from this study may promote the wide development of safe and cost-efficient self-healing composites in aeronautical, automotive, civil engineering and wind power industries.