Microencapsulated Self-Healing Composites

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ABSTRACT

The development of self-healing composites has allowed to overcome one of the current limitation of aeronautical materials, such as the absence of auto-repair mechanisms in composite structures. One of the most explored self-healing system for thermosetting resins is based on the use of an epoxy precursor, a microencapsulated healing agent and a catalytic chemical trigger within a thermoset matrix. This contribution deals with current limitations of self-healing materials based on olefin metathesis polymerization activated by Ru-initiators. In particular, a detailed evaluation of results concerning reactions of ring opening metathesis polymerizations (ROMP) initiated by ruthenium complexes has been carried out. New solutions have been proposed to optimize the effectiveness of the self-healing function in aeronautical resins. Among these, the chemical structure of a new initiator able to activate self-healing mechanisms has been proposed. The catalyst is a ruthenium based complex active in the ROMP reaction of cyclic olefins which, for its high thermal and chemical stability, can be used as molecular complex solubilized inside the epoxy precursors. It is worth noting that self-healing resins based on microencapsulated systems are inspired by a design proposed by White at al. [1]. In this kind of system, a rupture into the matrix causes cracks on the embedded vessels (microcapsules, microtubes etc...), thus allowing them to release a polymerizer agent into the crack plane. When the healing agent contacts the catalyst, the Ring Opening Metathesis Polymerization is triggered and the crack faces are bonded. The most efficient catalysts for this kind of system are the Hoveyda-Grubbs' second generation (HG2) complex and many catalysts belonging to this class of compounds have been tested in different epoxy matrices [2-8]. Recently, a new HG2 catalyst has been synthesized [9], characterized by a high thermal and chemical stability and able to activate metathesis reactions inside highly reactive environments of thermosetting epoxy resins. A very relevant advantage of this new initiator is the possibility to maximize the frequency of contact between initiator and epoxy matrix. In fact, whenever the liquid healing agent contacts the matrix, the metathesis reaction is activated because the initiator is not in form of particles, but in completely solubilized form. This overcomes statistical problems related to the possibility of contact between the initiator particles (dispersed in the thermosetting matrix) and the healing liquid flowing from the microcapsules. Furthermore, due to the peculiar initiator stereochemistry, the self-responsive function has proven to be very effective even after curing cycles typical of aeronautical materials.

The results of the performed activity highlight that the efficiency of this complex is closely related to its stereochemistry, which influences the ability of the catalyst to activate metathesis reactions within the material, also after a curing cycle up to 180°C. Aeronautic composites designed for primary structures are subjected to curing cycles at high temperatures, because these processing conditions are able to impart good machanical performance to the material. In this research work, metathesis tests and FTIR spectroscopy have been used to

highlight the important role of the catalyst' stereochemistry in the activation of self-healing mechanism. In particular, the different spatial orientation of phenyl groups in the N-heterocyclic carbene ligands of the new Hoveyda Grubbs' second-generation catalyst (see Figure 1) plays a key role. In fact, this complex with the *syn* spatial orientation of the phenyl groups, $HG2_{MesPhSyn}$ is able to promote self-healing mechanism, because it does not decompose after the curing process at very high temperature and in presence of aromatic primary amines as curing agent. On the contrary, the $HG2_{MesPhAnti}$ complex, with the *anti*-orientation of the phenyl groups, is deactivated in these conditions and then it is not able to activate metathesis reactions. The comparison carried out in this work, by means of FT-IR investigation and metathesis tests, highlights the potentiality of this new Ruthenium catalyst to impart self-healing function to aeronautic resins.

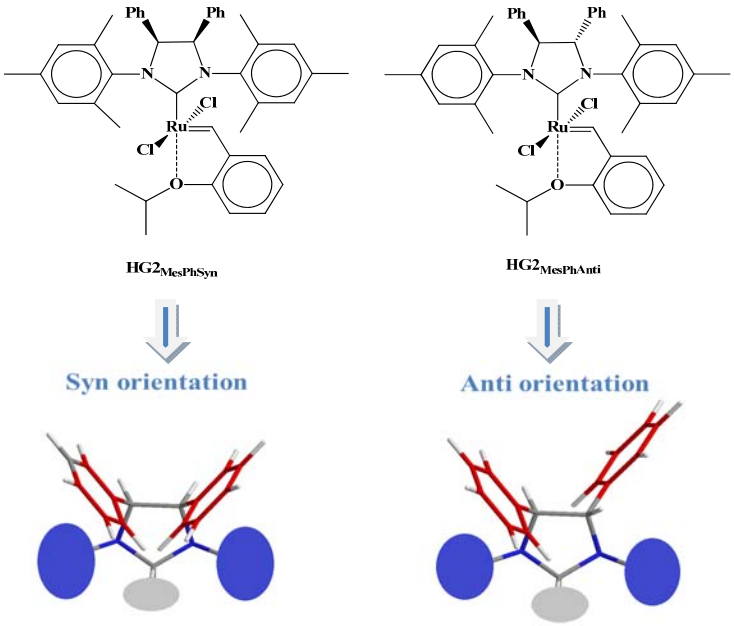

Figure 1: Chemical formulas of $HG2_{MesPhSyn}$ and $HG2_{MesPhAnti}$ complex

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References

[1] S.R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, and S. Viswanathan, Autonomic healing of polymer composites. *Nature*, **409**, 794-797, 2001.
[2] L. Guadagno, P. Longo, M. Raimondo, C. Naddeo, A. Mariconda, A. Sorrentino, V. Vittoria, G. Iannuzzo, and S. Russo, Cure behavior and mechanical properties of structural self-healing epoxy resins. *Journal of Polymer Science*, Part B: Polymer Physics, **48**, 2413-2423, 2010.
[3] W. H. Binder, *Self-Healing Polymers. From Principles to Applications,* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 1-425, 2013.
[4] M. Raimondo, and L. Guadagno, Healing Efficiency of Epoxy-Based Materials for Structural Applications. *Polymer Composites*, **34**, 1525-1532, 2013.
[5] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo and A. Mariconda, Self-healing materials for structural applications. *Polymer Engineering & Science*, **54**, 777-784, 2014.
[6] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, A. Mariconda and W.H. Binder, Healing efficiency and dynamic mechanical properties of self-healing epoxy systems. *Smart Materials Structures*, **23,** 11, 2014.
[7] M. Raimondo, P. Longo, A. Mariconda and L. Guadagno, Healing agent for the activation of self-healing function at low temperature. *Advanced Composite Materials*, **24**, 519-529, 2015.
[8] M. Raimondo, Self-repairing CFRPs targeted towards structural aerospace applications. *International Journal of Structural Integrity*, **5**, 656-670, 2016.
[9] P. Longo, A. Mariconda, E. Calabrese, M. Raimondo, C. Naddeo, L. Vertuccio, S. Russo G. Iannuzzo, and L. Guadagno, Development of a new stable ruthenium initiator suitably designed for self-repairing applications in high reactive environments. *Journal of Industrial and Engineering Chemistry*, **54**, 234-251, 2017.