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Development of a new stable ruthenium initiator suitably designed for self-repairing applications in high reactive environments

Pasquale Longo[a], Annaluisa Mariconda[a], Elisa Calabrese[b], Marialuigia Raimondo[b], Carlo Naddeo[b], Luigi Vertuccio[b], Salvatore Russo[c], Generoso Iannuzzo[c], Liberata Guadagno[b,*]

[a] Department of Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 132-84084 Fisciano,SA, Italy
[b] Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132-84084 Fisciano, SA, Italy
[c] Leonardo-Finmeccanica SpA, Engineering and Industrialization/New Airframe Technologies, Viale dell'Aeronautica, Pomigliano D'Arco, NA, 80038, Italy

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ABSTRACT

A stable initiator for ROMP reactions, suitably designed to be embedded in structural resins, has been synthetized. It rapidly polymerizes cyclic olefins in reactive environments. The thermal stability and chemical inertness towards oxirane rings allow its employment in the form of molecular complex in epoxy precursors thus reducing the amount of initiator in structural self-healing materials of 90% wt/wt, simultaneously preserving the catalytic activity at high temperatures (180–200 °C) also in presence of the aromatic primary amine (DDS). NMR and FTIR spectroscopy highlighted a relevant initiator stability able to fulfill industrial requirements. Self-healing efficiency has been found to be 103%.

Introduction

Inspired by living systems, self-healing materials are characterized by intrinsic ability to autonomically repair damage, thus providing a means to significantly extend the service life and reliability [1–3]. Several conceptual approaches have been explored to integrate self-healing ability in different materials depending on their nature. Self-healing mechanisms integrated in thermosetting resins have been extensively studied [4–16]. Recently, a range of epoxy blends were investigated to evaluate mechanical properties and suitability for use as healing agents for the repair of fibre-reinforced polymer (FRP) composites [16]. In order to determine the effectiveness of the healing resins, FRP specimens were designed to encourage the controlled formation of damage which can be repaired by infusion of the resin blends. It has been found that the toughened epoxies were capable of providing complete recovery of stiffness [16]. Generally, the more studied approaches for autonomic self-healing of thermoset-based materials involve incorporation of self-healing agents within a brittle vessel prior to addition of the vessels (microcapsules, nanotubes, vascular network etc.) into the polymeric matrix [4,8–21]. Using the ROMP reaction, White et al. were able to self-heal the cracks in thermoset material based on microencapsulated system [4]. Other self-healing materials using microencapsulated systems were recently tested by Chung et al. [22] and Cho et al. [23]. In Ref. [22], the authors used the monomer dimethylphenol (DMP) and styrene-butadiene-styrene triblock copolymer (SBS) rubber as healing agent. These components were used as core material to manufacture microcapsules incorporated into manufacturing self-healing asphalt. The healing mechanism was hypothesized due to a polymerization of DMP into poly (phenylene oxide) PPO by metals already existing in asphalt and the catalytic action of oxygen molecules in the air [22]. Cho et al. developed microencapsulated systems where the healing agent was a mixture of polydimethylsiloxane and polydiethoxysiloxane with hydroxyl end group and the catalyst was di-*n*-butyltin dilaurate able to heal microcracks on metal surface by condensation polymerization [23]. Supramolecular chemistry which utilizes multiple, reversible, and in certain cases, cooperative intermolecular interactions can be advantageously exploited to create new materials with unique properties and functionalities [24–26]. Reversible coordination abilities of polyphenols to metal ions can be useful employed to impart self-healing behavior to novel conjugate hydrogels [27].

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* Corresponding author.
E-mail address: lguadagno@unisa.it (L. Guadagno).

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Ring-opening metathesis polymerization (ROMP) has provided a powerful means for enabling self-healing mechanisms in epoxy systems for structural application [1,4,28–38].

However, ROMP initiators suffer from a lack of functional-group tolerance [28–32], which can limit their applicability to activate self-healing mechanisms in structural materials. In fact, although in the last years, the implementation of ruthenium catalyzed olefin metathesis has benefitted from a broad functional group tolerance, as for the development of *N*-heterocyclic carbene ruthenium initiators [39–43], nitrogen bases, as the DDS hardener which is employed for the curing of high performance structural materials, have remained challenging often-requiring initiator protection [44]. One of the most promising extrinsic ROMP-based self-healing system for structural materials was firstly proposed in the year 2001 by White et al. [4] and constituted a significant break-through and milestone in self-healing chemistry which allowed self-repair mechanisms for thermosetting polymers to grow rapidly over the past decade. These systems incorporate vessels containing healing agent (microencapsulated dicyclopentadiene (DCPD) or microvascular network etc.) and a catalytic chemical trigger within an epoxy matrix (usually EPON 828). The microcapsules usually have been prepared via a urea-formaldeyde (UF) polycondensation [45]. A rupture would cause cracks on the embedded microcapsules, thus allowing them to release a polymerizer agent into the crack plane. Polymerization of the healing agent is realized through Ring-opening metathesis polymerization (ROMP) which is triggered by contact with the embedded initiator and bonds the crack faces. Although some progress has been made in implementing the first proposed epoxy systems, most of the repair mechanisms are still based on ROMP reactions. Studies have been carried out using Grubb's first-generation initiator (G1) and other ruthenium initiators [7,8,18,46–49]. These systems allow to impart auto-repair function to epoxy resins. However, several drawbacks still need to be considered for more advanced applications where high mechanical performance is required (aircrafts, ships, wind turbine blades, satellite control boards etc.). In particular, the epoxy formulations designed for high-performance mechanical polymers require a minimum value in the glass transition temperature (Tg) (after wet aging) of 170 °C–180 °C. This value in Tg of the resin can be obtained only using as "hardener agents" aromatic primary and secondary amines. Furthermore, the processing conditions able to impart high mechanical performance to the material usually require curing cycles also up to 180 °C during the curing of the resin. High temperatures and very reactive environments (such as epoxy resins) cause deactivation or thermolytic decomposition of the ROMP initiators, which in turn limit the efficiency of self-healing function. As mentioned before, another critical point is related to the curing agent employed to solidify the epoxy system. Primary and secondary amines and most of all aromatic primary amines impose severe limits in the applicability of the self-healing chemistry based on ROMP reactions because they deactivate the ROMP initiators even at low temperatures (in the phase of preparation of the self-healing mixture). In order to overcome this drawback, the hardener ancamine or other tertiary amines have been used to solidify the matrix hosting ROMP initiators. Although tertiary amines allow to formulate self-healing systems, there is a limit in max value of Tg due to the curing mechanism of tertiary amines because the final result is a polyether (see electronic Supporting information (ESI)—Section 1).

For example, the epoxy matrix composed of EPON 828 (the more common bifunctional epoxy precursor) hardened with diethylenetriamine (DETA) is unable to host initiators for ROMP reaction because the hardener deactivates the initiator [9,10,50]. Paraffin wax has since been used to avoid the initiator deactivation [10]. However, the plasticization of polydicyclopentadiene (PDCPD) formed in the crack plane during healing and the thermal stability of paraffin wax pose limitations on the application in which ROMP-based self-healing polymers can be used.

In recent publications, critical issues have been highlighted in the use of epoxy precursors in conjunction with Hoveyda–Grubbs' II (HG2) metathesis initiator [7], as well as in the healing efficiency of self-healing epoxy formulations hardened at 170 °C–180 °C, when Hoveyda–Grubbs' I (HG1) metathesis initiator is employed [11].

Ethylene norbonene (ENB) and Hoveyda Grubbs I (HG1) initiator particles were used as self-healing components, and in-situ measurements of the healing efficiency, on tapered double-cantilever beam (TDCB) specimens, provided very high values (even higher than 100%). More specifically, the healing efficiency has been found to be affected by the concentrations and morphological parameters of both the microcapsule and the initiator. Self-healing technologies for structural materials, able to repair the damage at macro-scale [14], thus effectively preventing the propagation of the impairment and ultimately extending the lifetime of the material, have been already proposed in literature.

Despite the positive results on the healing efficiencies, for specific industrial applications, the performance related to several mechanical properties has been found lacking due to the impracticality of introducing aromatic primary amines in the developed self-healing epoxy formulations, as these deactivate the ROMP initiators also using different strategies to preserve the initiator [7].

No self-healing thermosetting materials based on ROMP mechanisms (microencapsulated systems or systems with microvascular networks) hardened with primary aromatic amines have been proposed until now in literature. Experiments have been performed highlighting that, when initiator particles are solubilized at molecular level (to reduce the cost of the self-healing materials), the particles which are in contact with the oxirane rings (during the curing reactions) are deactivated, hence reducing the actual amount of the active initiator. The deactivation also occurs in presence of tertiary amines (then in absence of primary and secondary amines) when ROMP initiators are solubilized at molecular level in epoxy precursors hardened at high temperature (up to 180 °C). Experiments performed on this issue showed that an equimolecular reaction between the epoxide ring and the alkylidene of the ruthenium compound causes the deactivation of the ROMP initiator [15]. It was therefore concluded that it is only possible to enable self-healing reactions in epoxy matrices when cured at high temperature (130 °C–170 °C) using solid initiator particles; these retain an intact "heart" of initiator which is not deactivated when in contact with the oxirane rings of the epoxy matrix. Appropriate curing cycles able to open the oxirane rings before the equimolecular reaction between epoxy ring and initiator have been described in a recent patent, but also in this last case, no aromatic primary amines have been used to solidify the epoxy mixture [51].

In summary, metathesis initiators developed until now to manufacture self-healing epoxy resins of composite structures have proven to be affected by two relevant drawbacks: 1) poor mechanical performance of the developed materials and 2) production cost not suitable for industrial production. Concerning the point 1), the developed systems (containing the ROMP initiators) do not meet the mechanical requirements suggested by many industrial manufacturers for specific applications (aircrafts, ships, wind turbine blades, satellite control boards, etc.). The poor mechanical performance of the microencapsulated systems has been found due to: a) the impossibility to use hardeners as aromatic primary amines (e.g. DDS) in combination with initiators active in the Ring Opening Metathesis Polymerization (ROMP); b) the impossibility to use curing cycles at high temperatures as those scheduled for materials designed for load-bearing structures.

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