Synthesis of ruthenium catalysts functionalized graphene oxide for self-healing applications

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ABSTRACT

Graphene Oxide (GO) was prepared by chemical oxidation of high surface area graphite (G). GO was used to support ruthenium catalysts with the aim to activate self-healing reactions in multifunctional materials able to integrate simultaneously the healing reactions with the very interesting properties of graphene-based materials.

Grubbs catalysts 1st (G1) and 2nd generation modified (G2$_{o\text{-tol}}$), Hoveyda-Grubbs catalysts 1st (HG1) and 2nd generation (HG2) were covalently bonded to GO preserving the same catalytic activity of the catalysts not bonded to the graphene sheets. GO-G2$_{o\text{-tol}}$ and GO-G1deactivate during the process of preparation of the self-healing epoxy mixtures at 90 °C. Evidence of the self-healing activity of the various catalytic complexes was investigated for both uncured and cured samples. Results show that GO-HG1 and GO-HG2 are not deactivated and hence they are able to trigger self-healing reaction based on the ROMP of 5-ethylidene-2-norbornene (ENB). This behavior is most likely due to the formation of 16 electron Ru-complexes that are more stable than the 14 electron complexes of GO-G1 and GO-G2 catalysts.

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1. Introduction

In recent years, material scientists are taking a big step towards design and development of new structural materials in several industrial fields. For example, in aeronautics, new solutions have been proposed to improve safety and help to get, through fuel savings, environmental and economic benefits by use of lighter, stronger and more rigid polymer composites. These materials have already been applied in aircraft structures to replace the traditional metal alloys. However, in order to achieve the necessary mechanical strength for many structural applications, highly cross-linked polymeric materials are needed. Cross-linked polymers tend to be brittle and they are subject to structural weakening due to the impact damage that can lead to substantial matrix micro-cracking, delamination and fiber-matrix de-bonding, with a consequent reduction of the structural capability. Self-healing thermosetting resins are able to limit the fatigue damage and preserve their

integrity, increase their lifespan, reduce maintenance costs, and ensure safety of passengers and staff [1].

Smart materials for structural applications capable to self-repair are widely studied and developed. The first thermosetting system with self-healing ability was proposed by White et al. [2] which formulated and characterized a multifunctional autonomically healing composite based on microencapsulated dicyclopentadiene and Grubbs' catalyst embedded in the polymer matrix. This system proved to be capable of responding to propagating fatigue cracks by autonomic processes that lead to higher endurance limits and life extension, or even the complete arrest of the crack growth [3]. When a crack is formed in the polymeric matrix of these systems, embedded microcapsules are ruptured by this crack growth, which then release the dicyclopentadiene into the crack plane through capillary action. Ring opening metathesis polymerization (ROMP) of the dicyclopentadiene is triggered by contact with the suspended catalyst phase. As the healing reaction progresses, the crack plane fills with polymerized dicyclopentadiene leading to the retardation or permanent arrest of further fatigue crack propagation [3–5].

Besides the DCPD [2,6] several self-healing agents were used within the microcapsules, *i.e.*: 5-ethylidene-2-norbornene (ENB), blends of DCPD/ENB or DCPD/5-norbornene-2-carboxylic acid [7]. Furthermore, also other catalytic systems in addition to the Grubbs first generation [8–11,2,12] for ring-opening metathesis polymerization-based self-healing applications have been evaluated, *i.e.*: Grubbs' second generation (G2) [7] and Hoveyda–Grubbs' first [7,13] and second generation [7,14] (HG1 and HG2, respectively).

Many papers dealing with several aspects on the choice of the healing agent, healing efficiency, curing degree of the epoxy matrix, distribution and deactivation of the catalyst in the polymeric matrix have been recently published [13,15–17].

However, there are still a number of unresolved problems: the high amount of ruthenium based catalyst used in the formulation of the composite material (weigh upon for 5% by weight), its high market price and the need to impart additional functionalities to the epoxy matrix.

In this paper, in the attempt to significantly reduce the amount of metathesis catalyst and increase at the same time the properties of the epoxy matrix, ruthenium catalysts for ring opening metathesis polymerization (ROMP) were covalently bonded to graphene oxide. Many recent works highlight the significant benefits due to graphene nanoparticles embedded in the polymeric matrix of structural materials [18–29].

Graphene exhibit fascinating physical properties such as thermodynamic stability, extremely high charge carrier mobility and mechanical stiffness, critical requisites for several applications [18–24]. Moreover, graphene based materials can activate self-assembling mechanisms able to improve gas barrier and mechanical properties of nanocomposites [25,26]. Furthermore, a large increases of the glass transition temperature of the nanocomposite can be observed in presence of GO [27].

To satisfy the above several requirements and impart self-healing capabilities to multifunctional materials, GO was prepared by chemical oxidation of graphite and ruthenium based catalysts have been covalently bonded on graphene oxidized, in this way the quantity of catalyst could decrease significantly and the presence of functionalized GO can have the beneficial effects of GO on the properties of the epoxy matrix.

Ru catalysts covalently bonded to graphene oxide were tested in reactions of ROMP of 2-norbornene and 5-ethylidene-2-norbornene which is a healing agent recently proposed in literature for thermosetting self-healing formulations [13–17]. Graphene based catalysts were embedded in the epoxy precursors used for structural resins and the first experiments on the evaluation of their catalytic activity were performed. Tests on the evaluation of the crack-healing efficiency of the developed self-healing materials, after the curing treatment, were carried out using Dynamic Mechanical Analysis (DMA). Very promising results were obtained for GO-HG1 and GO-HG2 catalysts.

2. Experimental section

2.1. Materials and methods

#### 2.1.1. Preparation of graphene oxide (GO)

A method for large-scale fabrication of graphene oxide was chosen for eventual future industrial application. One of the most common large-scale preparation method is the Staudenmaier's method [30]. This procedure starts with the oxidation of graphite (G) to graphene oxide (GO) using concentrated acids (concentrated sulfuric acid H_2SO_4 in combination with fuming nitric acid HNO_3 and potassium chlorate $KClO_3$).

The GO used for this work was prepared starting from the high surface area graphite (G) (trade name Synthetic Graphite 8427) from Asbury Graphite Mills Inc., with a minimum carbon wt % of 99.8 and a surface area of 330 m^2/g [31].
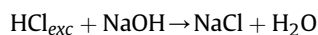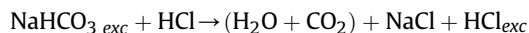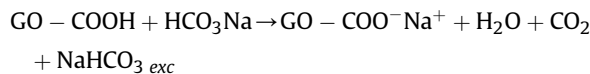
A 2000-mL three-neck flask was flushed with gaseous N_2 and then immersed into an ice bath. G (30 g) was added to a homogeneous mixture of 200 mL of nitric acid and 400 mL of sulfuric acid under vigorous agitation. After the uniform dispersion of G powders, 250 g of potassium chlorate were added very slowly to minimize the risk of explosion. The reaction mixture was allowed to go on for 120 h at room temperature. The resulting dark green slurry was poured into a copious amount of a 5 wt % HCl aqueous solution and then centrifuged at 10,000 rpm for 15 min (Hermle Z 323 K). The GO powders were further washed with a 5 wt % HCl aqueous solution (2 × 100 mL) and deionized water and finally vacuum dried in an oven at 60 °C for 48 h.

2.1.2. Quantitative evaluation of the −COOH groups on GO

The acidity of the GO was determined performing a typical acid-base titration. Amount of carboxyl and total acidic site on the GO were quantitatively chemical analyzed by titration. 50 mg of GO were dispersed in 50 ml of NaOH (0.05 M) and all this was sonicated for 30 min to obtain the complete reaction between acid group and the base and to remove CO_2. The excess of NaOH was titrated with HCl (0.05 M) and the variation of pH (pH meter Mettler toledo) was registered after subsequent addition of 1 ml of acid. The equivalent volume (V_{eq}) that allows to determine the moles consumed and the title was obtained from the point of inflection. The title obtained for difference was 14.1 mmol/g.

$$GO - OH + NaOH \rightarrow GO - O^- Na^+ + H_2O + NaOH_{exc}$$

$$NaOH_{exc} + HCl \rightarrow NaCl + H_2O$$
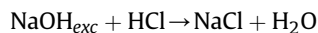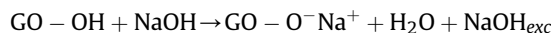
A second titration was conducted at the aim of value the only carbossilic acid group using a more weak base $NaHCO_3$. 50 mg of GO were dispersed in 50 ml of $NaHCO_3$ (0.05 M) and were sonicated for 30 min 50 ml of acid solution (HCl 0.05M) were added into the flask. The excess of HCl was slowly titrated with NaOH (0.05 M) and the variation of pH was registered after subsequent addition of 1 ml of acid. The value of the title was found to be 5.5 mmol/g.

$$GO - COOH + HCO_3Na \rightarrow GO - COO^- Na^+ + H_2O + CO_2 + NaHCO_{3\ exc}$$

$$NaHCO_{3\ exc} + HCl \rightarrow (H_2O + CO_2) + NaCl + HCl_{exc}$$

$$HCl_{exc} + NaOH \rightarrow NaCl + H_2O$$

Titrations were performed in triplicate.

2.2. Functionalization of graphene oxide with ruthenium based catalysts

Grubbs catalysts 1st (G1) and 2nd generation modified (G2$_{o\text{-tol}}$) and Hoveyda-Grubbs catalysts 1st (HG1) and 2nd generation (HG2) were covalently bonded to the graphene oxide sheets.

Fig. 1 shows the chemical formulas of the catalysts which were covalently bonded to the GO.

2.2.1. First step

6200 mg of dried GO were added in a 500 mL schlenk flask together with 300 mL of thionyl chloride under nitrogen. The suspension was stirred for 48 h at reflux under nitrogen. The excess of thionyl chloride was evaporated under vacuum. FT/IR spectrum