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Use of Hoveyda–Grubbs' second generation catalyst in self-healing epoxy mixtures

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ABSTRACT

The development of smart composites capable of self-repair on aeronautical structures is still at the planning stage owing to complex issues to overcome. A very important issue to solve concerns the components' stability of the proposed composites which are compromised at the cure temperatures necessary for good performance of the composite. In this work we analyzed the possibility to apply Hoveyda–Grubbs' second generation catalyst (HG2) to develop self-healing systems. Our experimental results have shown critical issues in the use of epoxy precursors in conjunction with Hoveyda–Grubbs' II metathesis catalyst. However, an appropriate curing cycle of the self-healing mixture permits to overcome the critical issues making possible high temperatures for the curing process without deactivating self-repair activity.

1. Introduction

Polymeric composites are used to replace the traditional metal alloys. These materials, however, are subject to weakening through impact damage which can lead to substantial matrix micro-cracking, delamination and fibre–matrix de-bonding, resulting in the reduction of structural capability. If damage is not detected and repaired, the result will be premature failure. Airlines, however, see polymeric composites' potential to cut fuel costs and save on maintenance very attractive, therefore, are willing to entertain the idea to put into action self-healing composites in aeronautical applications. The challenge facing materials scientists is to assure these systems must be able to stem fatigue damage and preserve their integrity, increase their life span, reduce maintenance costs and provide safety during use. A lot of strategies were formulated in the development of self-healing materials [1–14]. The right strategy to manufacture a thermosetting self-repair material seems to be the storage of healing agents inside composites that restore the strength of the materials after damage. A very interesting autonomic self-healing system for thermosetting materials, in terms of design, was recently proposed by White et al. [8]. This system consists of incorporating a microencapsulated healing agent and a catalytic chemical trigger within an epoxy matrix [8–14]. An approaching crack ruptures embedded microcapsules releasing a polymerizer agent into the crack plane through capillary action. Polymerization of the healing agent is triggered by contact with the embedded catalyst, bonding the crack faces. In these systems the efficiency of self-repair function, in terms of trigger, speed and yield, is related to ring-opening metathesis polymerization of the healing agent by appropriate catalysts. The healing agent is a microencapsulated liquid monomer that must include a long shelf life, prompt deliverability, high reactivity, and low volume shrinkage upon polymerization [15]. The monomer most often used as the healing agent for the manufacture of these first ingenious systems is dicyclopentadiene (DCPD) [8,15]. Very recently, however, blends of DCPD/5-ethylidene-2-norbornene (DCPD/ENB) or DCPD/5-norbornene-2carboxylic acid have also been proposed [16]. Thermosetting auto-repair polymers, which have been proposed so far, include Grubbs' first-generation catalyst (G1); [2,3,6–8,12] and currently, the possibility of applying other ruthenium catalysts for ring-opening metathesis polymerization-based self-healing applications is being evaluated. In a recent paper, the dissolution properties, initial polymerization kinetics, chemical stabilities, and thermal stabilities were analyzed for three catalysts: Grubbs' first (G1) and second generation (G2) catalysts and Hoveyda–Grubbs' second generation catalyst (HG2) [16]. Regarding Hoveyda catalysts, until now the experimentation was focused on the second generation catalyst because it has demonstrated impressive chemical stability and recyclability [16–18].

Ruthenium-based catalysts are reported as exhibiting great functional group tolerance, as well as greatly enhanced air and water stability [19]. However, thermolytic decomposition can limit

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the usefulness of these ruthenium systems in self-healing composites based on epoxy resins. This is a crucial aspect for self-healing systems in aeronautic applications because, even if linked to the cost reduction from a process aspect, resins have been developed with low temperature manufacturing (under 100 °C), yet the problem of the material treatment at high temperature is not resolved. In fact, we generally need a glass transition temperature after wet aging of 110 °C minimum, and a curing temperature equal to or less than 100 °C is not enough. To achieve this goal it is necessary to make a post cure with a temperature that could be as high as 180 °C. For this reason, we have carried out our investigation in the temperature range of 150–180 °C.

In particular, it is worth noting that our experimental results have shown critical issues in the use of epoxy precursors in conjunction with Hoveyda–Grubbs' II metathesis catalysts, because in self-healing composites based on epoxy resins, ruthenium systems give rise to a reaction with the oxirane rings of the epoxy precursors, and, therefore, the metathesis catalyst was not subsequently able to promote the polymerization of the reactive monomer, thus losing the self-healing ability. Such phenomena could strongly limit the use in the practice, in self-healing composite materials, of Hoveyda–Grubbs' II catalyst, preventing a proper exploiting of the excellent intrinsic properties of the latter.

In this work we analyzed the possibility to apply Hoveyda–Grubbs' second generation catalyst (HG2) to develop efficient self-healing systems. We have performed some experiments, which have allowed to obtain the unprecedented results to preserve the catalytic activity of HG2 in self-healing composite materials.

In particular, selecting the appropriate curing cycle as well as the specific chemical formulation the catalyst remains intact in the formed epoxy matrix during the curing process, and is thus capable of subsequently performing its catalytic activity of the polymerization of the reactive monomer consisting in the cyclic olefin (5-ethylidene-2-norbornene –ENB–), when the latter comes out of a microcapsule affected by a crack.

2. Experimental

2.1. Materials

The epoxy matrix composite was prepared by mixing an epoxy (trade name EPON 828 – Acronym DGEBA) with an epoxy flexibilizer (Dimer Acid Diglycidyl Ester – trade name HELOXY 71 – Acronym DADGE) which was used in small percentage to improve the toughness of the material and consequently crack growth stability. These resins, both containing an epoxy, were obtained by Sigma–Aldrich.

The curing agent investigated for this study is an anionic initiator Phenol, 2,4,6-tris[(dimethylamino) methyl] (Trade name Ancamine K54). Hoveyda–Grubbs' second generation catalyst obtained from Aldrich was used to manufacture the epoxy matrix. It was reduced in the form of thin powders before dispersion into the epoxy matrix.

2.2. Thermal stability of ring-opening metathesis catalyst

Thermal stability of ring-opening metathesis catalyst (HG2) was verified introducing ~20 mg of ruthenium compound in a vial, which was kept for the time of the run 3 h at 150 °C (run 1) or 1 h at 180 °C (run 2). Then the solid was dissolved into 0.5 ml of $CDCl_3$ and analyzed by ^1H NMR.

2.3. Epoxy specimens manufacture

Sample EHA was obtained by mixing Epon 828 with Heloxy 71 flexibilizer at a concentration of 63%:37% (by wt) epoxide to flexibilizer. Ancamine K54 was added at a concentration of 10:100 (by wt) hardener to mixture (Epon 828 and Heloxy 71). The Epoxy matrix for the potential use as self-healing material was obtained homogeneously dispersing finely pulverized Hoveyda–Grubbs' catalyst HG2 (5 wt.%) into the EHA sample. This last mixture was cured by a single or two-stage curing cycle. For two-stage curing cycles, a first isothermal stage was carried out at lower temperature for 2 h and the second isothermal stage at higher temperatures up to 180 °C; these samples are named EHA-HG2(Y) where Y is the temperature of the second stage.

2.4. Characterizations

^1H NMR spectra were recorded on an AV300 Bruker spectrometer, using $CDCl_3$ as solvent and tetramethyl silane as internal reference.

Infrared spectra were performed at room temperature by using a Bruker Vertex 70 FTIR-spectrophotometer with a 2 cm^{-1} resolution (64 scans collected).

3. Results and discussion

3.1. Evaluation of catalyst thermal stability by ^1H NMR and FT/IR

Thermal stability of the catalyst HG2 was evaluated in air and under conditions of actual use for applications in self-healing structural systems. In this last case, the catalyst is dispersed into the epoxy matrix in its solid state and the mixture was cured (with the curing agent) choosing processing conditions that contemplate permanence at high temperatures; after which, the catalyst was extracted from the epoxy matrix and analyzed by ^1H NMR spectroscopy. Infrared spectroscopy was used to evaluate the catalytic activity directly inside the epoxy resin after the cure processing.

3.2. Nuclear magnetic resonance (NMR) spectroscopy

^1H NMR analysis was carried out for monitoring and estimating the catalyst stability. In the spectra of Hoveyda–Grubbs' second generation catalyst (HG2), the presence of the characteristic resonance signal of the benzylidene carbene proton can be considered for directly assaying the state of the catalyst. ^1H NMR spectrum of (HG2) catalyst shows, at room temperature, the signal of Ru = CH-Ph at 16.6 ppm.

The thermolytic stability for this catalyst was evaluated in air atmosphere with the catalyst in powder form kept at different temperatures directly from the solid state, because it represents the same form in which is dispersed into the epoxy mixture to manufacture epoxy systems with self-healing function. The catalyst powder, after the thermal treatment, was dissolved in the deuterated solvent (deuterated chloroform – $CDCl_3$) immediately before the ^1H NMR spectrum recording (see Section 2).

HG2 catalyst shows exceptional stability also after a thermal treatment at 180 °C in air atmosphere (see experimental part). The stability of the catalyst was subsequently also analyzed for the powder embedded inside the epoxy matrix (after the curing process at high temperatures). In particular, the epoxy matrices containing the catalyst were cured by a two-stage curing cycle: a first isothermal stage was carried out at 125 °C for 2 h and the second isothermal stage at higher temperatures up to 180 °C for 2 h. In this case, as well as for samples directly cured at 150 and 180 °C we did not obtain HG2 by chloroform extraction. Evidently the performed tests determined that the use of HG2 catalyst in epoxy self-healing systems manufactured by a process curing up to 150 or 180 °C, deactivate the catalyst.

In order to verify that observed by NMR analysis, we performed some FT-IR experiments.

3.3. Infrared analysis

Infrared spectroscopy provides a useful way to identify metathesis products and therefore catalyst activity. To analyze the catalytic activity directly inside the epoxy resin after the cure processing, the epoxy matrix containing the catalyst was cured by a two-stage curing cycle: a first isothermal stage was carried out at 125 °C for 2 h and the second isothermal stage at the higher temperature of 170 °C obtaining the sample named EHA-HG2 (170). This sample was cut by a serrated blade; the powder which was produced from the sample was collected in a mortar and a drop of healing agent (5-ethylidene-2-norbornene – ENB) was added before dispersing the sample powder into the KBr disks for FTIR investigation.

Fig. 1 shows FTIR spectra of EHA-HG2 (170) powder treated with ENB. From the absence of the peak at 966 cm^{-1} characteristic of ring-opened poly(ENB) we deduce that the HG2 catalyst shows an inability to polymerize the ENB monomer, providing evidence that the embedded catalyst is inactive for a curing temperature of the epoxy formulation up to 170 °C. Similar results were obtained also for EHA-HG2 (150) sample with the curing cycle described in the experimental part.

In light of the results reported previously and in literature [16], which show for HG2 a high temperature of beginning degradation (∼225 °C), the unexpected results obtained by NMR and FT-IR analysis when the ruthenium based catalyst is treated in the epoxy matrix have spurred us to undertake an investigation aimed at understanding the reactivity of the catalyst inside the epoxy resins.

To verify if it is possible to extend the curing temperature up high temperatures, different tests were performed for systems with powder of Hoveyda–Grubbs' catalyst embedded in the epoxy formulation.

First we analyzed the behavior of the HG2 catalyst in the only epoxy precursor (Epon 828) at different temperatures. Fig. 2 shows FTIR spectra of a mixture obtained by dispersing the HG2 catalyst (5%) in the *Epon 828* epoxy precursor (EHG2-sample) and submitting this mixture to an increase of temperature between 100 °C and 180 °C for different treatment times, as reported in the figure legend.

It is worth noting that this sample is only obtained by mixing the epoxy precursor and the HG2 catalyst powders. No other components were added to the mixture, and in particular, no curing agent was mixed in the formulation. Fig. 2 highlights the most intense band of the epoxy ring at 916 cm^{-1} which is attributed to asymmetrical ring stretching in which the C–C bond is stretching during contraction of the C–O bond. In the initial spectrum, (EHG2–*100 °C, t = 0.00* h – red curve), the band at 916 cm^{-1} is very evident. The intensity of this peak decreases by increasing the treatment temperature. The peak completely disappears for a treatment time of 60 min at 150 °C. The resin treated at 150 °C for 1 or 2 h shows the same spectrum of the resin after a treatment at 180 °C (with a complete absence of the peak at 916 cm^{-1}).

These results suggest that the presence of the HG2 catalyst in the epoxy precursor involves a progressive and rapid disappearance of the signal to 916 cm^{-1}, even if no curing agent was blended into the mixture. Infrared spectroscopy can be then used to follow the curing process by determining the decrease of the band at 916 cm^{-1} due to the epoxy group [20]. In this case, where no curing agent is present, the decrease of the peak at 916 cm^{-1} can be attributed only to the reactions of the epoxy precursor oligomer with the catalyst powder. To confirm the interpretation validity of this last result the epoxy precursor **E** (without catalyst) was submitted to an increase of temperature between 100 and 180 °C under the same experimental conditions as the previous mixture (E-HG2). FTIR spectra of this sample are reported in Fig. 3. This last experiment was carried out to clarify if the decrease of the intensity peak at 916 cm^{-1} could be attributed to other independent factors from the presence of the catalyst, such as the possible polymerization reactions activated e.g. by free radicals due to the thermal degradation of the epoxy precursor.

Fig. 3 shows that the peak at 916 cm^{-1} is also very evident in the spectrum of the sample treated up to 180 °C. These last results point out that the flattening of the signal at 916 cm^{-1} observed in Fig. 2 for EHG2 samples cured between 150 and 180 °C can be ascribed to the effect of catalyst powder.

These results helped us understand why it was very difficult extraction of HG2 catalyst from the epoxy formulations and its

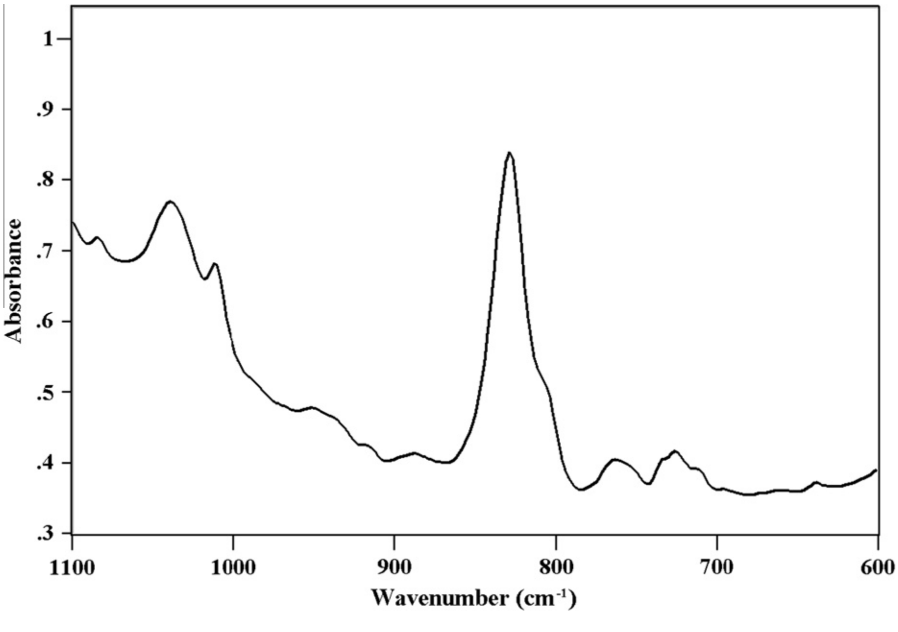

Fig. 1. FTIR spectrum of EHA-HG2 (170) powders treated with ENB.

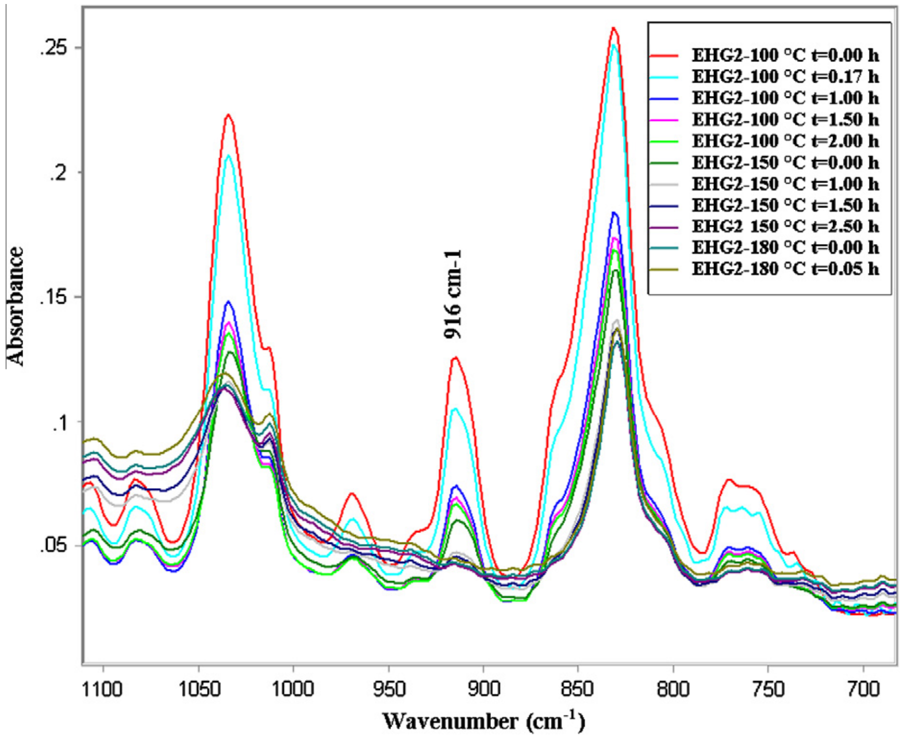

Fig. 2. FTIR spectra of EHG2 sample between 100 °C and 180 °C for increasing times. The highlighted peak at 916 cm^{-1} is characteristic of the oxirane ring.

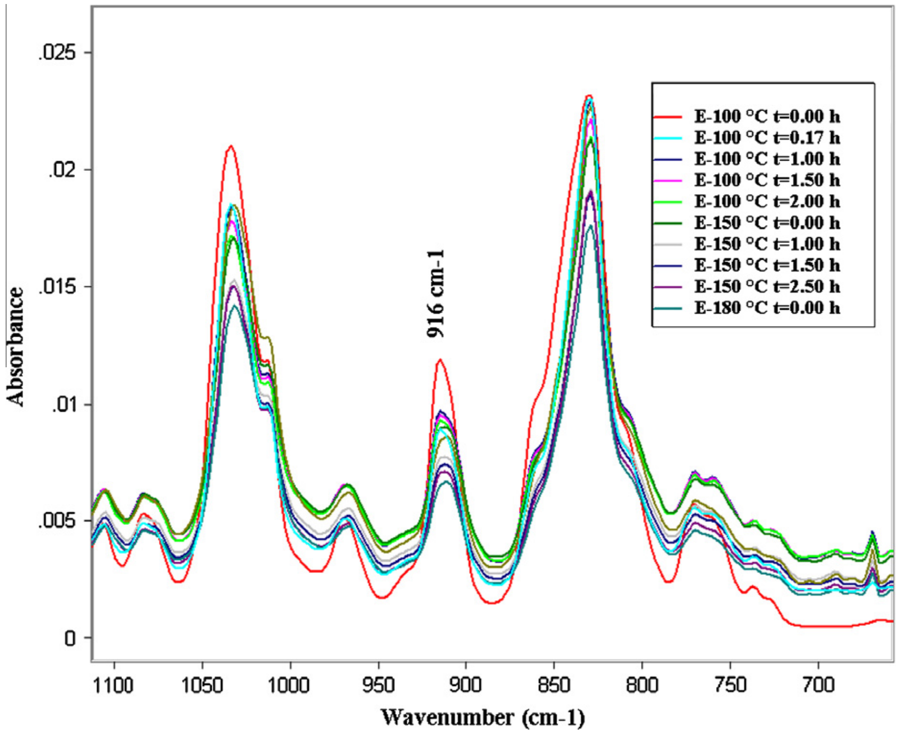

Fig. 3. FTIR spectra of E sample between 100 °C and 180 °C for increasing times.

ineffectiveness in the activation of the ring-opening metathesis polymerization. Probably, the catalyst extraction was impossible because it is chemically bonded to the epoxy matrix which also irreversibly changes its reactivity.

In this regard we have carried out experiments to better analyze the behavior of the epoxy groups with Hoveyda–Grubbs' II catalyst (see Supporting Information).

In light of our results, we attempted to preserve the HG2 catalyst complex from the formation of chemical bonds with the epoxy functionality. The idea put in practice was to use curing conditions that anticipate a passage of the epoxy formulation at low temperatures to open all the oxirane rings under conditions in which the catalyst HG2 is not reactive, for example at 70 °C. As it has been verified by our experiments, the HG2 catalyst does not react with

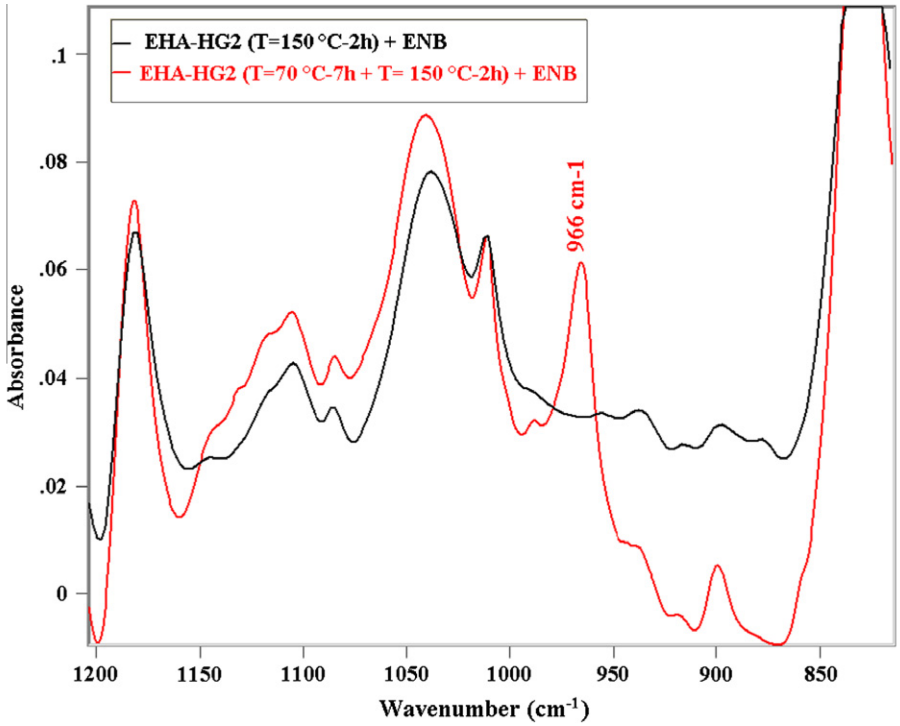

Fig. 4. FTIR spectra of EHA-HG2 sample after two different curing process: (a) a single stage directly at high temperature (2 h at 150 °C) black spectrum and (b) a pre-treatment at 70 °C for 7 h and the following treatment at 150 °C for 2 h (red spectrum). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the oxirane rings also for an extended time at this temperature. The temperature of 70 °C is high enough for the curing of a liquid epoxy formulations with many catalytic curing agents which promote epoxy-to-epoxy or epoxy-to-hydroxyl reactions and do not themselves serve as direct cross-linking agents. Tertiary amines are in this class. This choice did not involve a change of the epoxy specimen formulation because a tertiary amine was used as curing agent to avoid poisoning the Hoveyda–Grubbs' catalyst.

An analysis of the stability of the catalyst HG2 in the epoxy precursor (Epon 828) (without cross-linking agent) at 70 °C for increasing time (from 0 up to 7 h) was also performed to evaluate the peak intensity of the oxirane ring in the FTIR spectra. From this experiment it was observed that the peak of epoxy functionality at 916 cm^{-1} is also present and well developed after a treatment of 7 h at 70 °C proving that the catalyst does not affect the oxirane rings.

Fig. 4 shows FTIR spectra of the formulation EHA with the HG2 catalyst after two different curing processes: (a) after a curing process directly carried out at high temperatures (2 h at 150 °C) black spectrum, (b) after a two-stage curing process composed of a pre-treatment at 70 °C for 7 h and a following treatment at 150 °C for 2 h (red spectrum). For this investigation the powder produced from the samples was treated with a drop ENB before dispersing the sample powder into the KBr disks as already described for same of the previous investigations.

The spectra reported in Fig. 4 show that a direct treatment at high temperatures deactivates the catalyst, whereas, a pre-treatment at lower temperatures preserves the activity of the catalyst, as it can be deduced from the peak at 966 cm^{-1} characteristic of the metathesis product, that is the ring-opened poly(ENB).

Our experimentation has also shown that, with this pre-treatment at lower temperatures, the catalytic activity of the HG2 catalyst can be preserved up to temperatures between 150 °C and 160 °C; other treatments at temperatures higher than 160 °C deactivated the catalyst.

4. Conclusions

We have investigated the possibility to apply Hoveyda–Grubbs' second generation catalyst (HG2) to develop efficient self-healing systems. Our data have shown that by choosing the appropriate curing cycle, the catalytic activity of HG2 in the ROMP reactions can be kept under control. In particular, the catalyst remains intact in the formed epoxy matrix during the curing process, and is thus capable of subsequently performing its catalytic activity of the polymerization of the healing agent (ENB) in applications where the healing agent comes out of the damaged microcapsules.

The interesting results obtained from the analysis of the ring-opening metathesis polymerization inside of the epoxy resin using HG2 catalyst are of general validity. These can be applied also for another proposed bioinspired coating/substrate design [15,21] which delivers a healing agent to cracks in a coating via a three-dimensional microvascular network in the substrate.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.compositesb.2010.10.011.

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