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# Rheokinetic evaluation of self-healing agents polymerized by Grubbs catalyst embedded in various thermosetting systems

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ABSTRACT

In self-healing polymers and composites, the activity of the embedded chemical catalyst within the thermosetting matrix is critical to healing efficiency. Rheological behavior of ring-opening metathesis polymerization (ROMP)-based healing agents, triggered by 1st or 2nd generation Grubbs catalyst suspended in various thermosetting resins, was investigated using an oscillatory parallel plate rheometer. Gel times for various healing agents were determined from the crossover of storage and loss moduli vs. time curves to indicate the activity of the ROMP reaction. Gelation of healing agents initiated by 1st generation Grubbs catalyst occurred faster than those triggered by 2nd generation catalyst. It is suggested that the dissolution rate of the catalyst by the healing agent is an important factor in determining the overall ROMP reaction rate *in situ*. Optical and scanning electron microscopic observations showed that the finer, rod-like solid particles of the 1st generation catalyst were distributed more homogeneously throughout the cured matrix. The effects of different healing agents and thermosetting matrix systems on the ROMP reaction are discussed in detail.

## 1. Introduction

A new class of biologically inspired, structural composite materials is emerging with the ability to sense and respond to damage in an autonomous fashion to mitigate failure [1]. These synthetic self-healing materials consist of microencapsulated monomer healing agents dispersed throughout a thermosetting matrix. Also mixed throughout the polymer matrix is a suspended catalyst phase. Self-healing is initiated by crack propagation through the microcapsules, which then release the healing agent into the crack plane. Subsequent exposure of the healing agent to the transition metal catalyst initiates a ring-opening metathesis polymerization (ROMP) in the crack plane to rebond the crack faces.

In the literature on self-healing polymers and composites, the primary matrix material in which microcapsules and chemical catalysts are embedded during processing is a diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and a room temperature curing agent, diethylenetriamine (DETA). The primary ROMP healing agent system employed is *endo*-dicyclopentadiene (*endo*-DCPD) which is triggered by 1st generation Grubbs ruthenium catalyst [1–5]. Ethylidene norbornene (ENB) and its blends with *endo*-DCPD were later introduced as healing agent candidates and these systems showed faster healing kinetics at a much lower loading of Grubbs catalyst compared to the *endo*-isomer of DCPD [6–8]. Also, blending of novel bicyclic ROMP crosslinking agents with DCPD and ENB has been shown to accelerate the reaction and results in a polymerized healing agent with a higher glass transition temperature due to its densely crosslinked molecular structure [9].

While the majority of the previous work has focused on systems with DGEBA/DETA matrices, the concept is applicable, in principle, to any thermosetting polymers which are susceptible to damage in the form of microcracks.

There are a wide variety of thermosetting resins and curing agents being used for polymer composites, including those for high performance structural composites, in which processing and curing occur at elevated temperatures. In order for the self-healing methodology to expand into these higher performance systems, it is worthwhile to investigate the survival of Grubbs catalyst when processed in various thermosetting resins and curing agents. In this report, a novel parallel plate rheological technique is used to investigate the ROMP kinetics of different healing agents triggered by 1st or 2nd generation Grubbs catalyst which has been embedded in various thermosetting resins.

## 2. Experimental

The rheological behavior of healing agent candidates was measured between oscillating parallel discs, where the bottom plate

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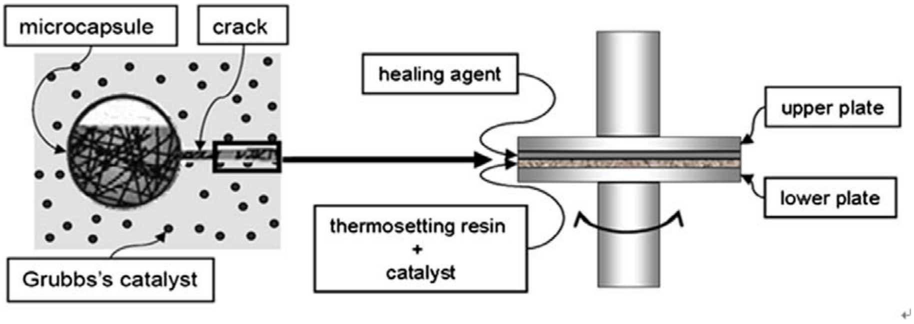

**Fig. 1.** Specimen configuration for rheology tests.

was coated with a cured thermosetting resin system embedded with catalyst as shown in Fig. 1. This method, which is similar to that used in our earlier work, is designed to simulate the *in situ* polymerization of the healing agent from fractured microcapules in a crack plane after the monomer contacts the catalyst in the matrix [7].

### 2.1. Thermosetting systems

The bisphenol-A type epoxy resin EPON-828 (DGEBA, Miller-Stephenson Chemical, USA) and the room temperature amine curing agent DETA (Miller-Stephenson Chemical, USA) was chosen as a benchmark matrix system since most of the previous work in self-healing composites used this matrix chemistry. The epoxy and curing agent were mixed at a stoichiometric ratio (DGEBA:DETA = 10:1 by weight) and an amine excess amount (DGEBA:DETA = 10:2 by weight) at room temperature (RT = 21 °C in all experiments) for 10 min using a magnetic stirrer. We tested the system with twice the stoichiometric amine ratio to evaluate the hypothesis that Grubbs catalyst looses its activity upon exposure to the amine group in the curing agent [3]. DGEBA was also blended with a high temperature curing agent, m-PDA (m-phenylenediamine, Sigma–Aldrich, USA) at 60 °C for 20 min. In addition, a high temperature cycloaliphatic epoxy resin (CA, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, Sigma–Aldrich, USA) was mixed with an anhydride curing agent (HHPA, hexahydro-4-methylphthalic anhydride, Sigma–Aldrich, USA) in the presence of initiator (EG, Ethylene glycol, Sigma–Aldrich, USA) and catalyst (DBA, *N*,*N*-dimethylbenzylamine, Sigma–Aldrich, USA) at RT for 10 min. Finally, an uncatalyzed bisphenol E type cyanate ester monomer (EX-1510, Bryte Technologies, USA) was also tested. The four different epoxy resin/curing agent systems and one cyanate ester resin evaluated as matrix materials in this study are listed, along with their cure conditions, in Table 1. Chemical structures of the thermosetting matrix resins and curing agents (and the healing agents, discussed below) are represented in Fig. 2.

### 2.2. Healing agent candidates

Dicyclopentadiene (DCPD, Acros Organics, Belgium), ethyledene norbornene (ENB, Sigma–Aldrich, USA), and ENB blended with two customized crosslinkers were investigated in this study as healing agent monomers. The loading with ENB for crosslinker 1 (CL1) was 10 wt% and crosslinker 2 (CL 2) was 5 wt%. The chemical structures of CL1 (which is a mixture of *exo*-, *endo*-isomer and *exo*-, *exo*-isomer) and CL2 are shown in Fig. 2. The synthetic schemes of the norbornene based crosslinkers are available in our previous published work [9].

**Table 1**
Thermosetting systems and their cure conditions used in this study

| Compositions (phr) | Cure conditions |
|---|---|
| DGEBA/DETA = 100/10 | RT × 16 h |
| DGEBA/DETA = 100/20 | RT × 16 h |
| DGEBA/m-PDA = 100/14.4 | 80 °C × 2 h/150 °C × 1 h |
| CA/HHPA/EG/DBA = 100/190/2.85/2.85 | 80 °C × 1 h/150 °C × 30 min |
| Cyanate ester (uncatalyzed) | 130 °C × 1 h |

### 2.3. Grubbs catalyst

Two generations of the catalyst, 1st, benzylidene-bis(tricyclohexylphosphine) dichlororuthenium and 2nd, benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine) ruthenium (Sigma–Aldrich, USA) were used as-received in this study. Both 1st and 2nd generation catalysts are tolerant of many functional groups and compatible with a wide range of solvents, and are also stable to air and moisture, which makes handling easy [10]. In self-healing applications, the suspended catalyst must remain active for ROMP with the healing agent after processing and curing of the thermosetting matrix.

### 2.4. Rheological measurements

A 5 wt% of 1st or 2nd generation Grubbs catalyst was mechanically dispersed in the various thermosetting matrix resins at 1200 rpm using a high shear mixer for 10 min at RT. The resin mixtures were coated on aluminum discs (diameter = 25.4 mm) with a controlled coating thickness of 0.18 mm. The coating thickness was controlled by first adhering the back side of the aluminum plate to a glass plate between two spacers. Approximately 0.4 g of the catalyst containing resin mixture was spread on the front side of the aluminum disc. Subsequently, the assembly was degassed in a vacuum oven for 20 min to remove air that was entrapped in the resin during mixing. Another glass plate was wrapped with Teflon® tape and placed onto the coated aluminum disc and spacers. The whole assembly was tightened with a rubber band and cured in a programmable oven using the cure conditions listed in Table 1. The coated disc was then used as the bottom plate in a parallel plate configuration (as shown in Fig. 1) for rheological measurements with a controlled strain oscillatory rheometer (ARES Rheometer, TA Instruments, USA). After the healing agent candidates were injected between the parallel plates and the gap between plates was properly set, the storage ($G'$) and loss ($G''$) moduli were collected every 3 s during reaction at RT. A frequency of 1 Hz and an oscillation strain of 6% were used for all experiments. For each coating, measurements were made three times after removing additional material (~0.03 mm) from the surface to expose fresh catalyst with sand paper.

### 2.5. Optical and scanning electron microscope

The morphology of 1st and 2nd generation Grubbs catalyst in the cured thermosetting matrix was observed with an optical