JOURNAL OF THE ROYAL SOCIETY Interface

Self-healing kinetics and the stereoisomers of dicyclopentadiene

Timothy C Mauldin, Joseph D Rule, Nancy R Sottos, Scott R White and Jeffrey S Moore

References	**This article cites 17 articles** http://rsif.royalsocietypublishing.org/content/4/13/389.full.html#ref-list-1 Article cited in: **http://rsif.royalsocietypublishing.org/content/4/13/389.full.html#related-urls**
Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

To subscribe to *J. R. Soc. Interface* go to: **http://rsif.royalsocietypublishing.org/subscriptions**

Self-healing kinetics and the stereoisomers of dicyclopentadiene

Timothy C. Mauldin[1,*]**, Joseph D. Rule**[1]**, Nancy R. Sottos**[2]**, Scott R. White**[3]
and Jeffrey S. Moore[1]

[1]*Department of Chemistry,* [2]*Department of Materials Science and Engineering, and*
[3]*Department of Aerospace Engineering and The Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL 61801, USA*

While original epoxy resin-based self-healing systems used the commercially available *endo*-isomer of dicyclopentadiene (DCPD), the *exo*-stereoisomer is known to have much faster olefin metathesis reaction rates with first-generation Grubbs' catalyst. Here, we measure the energy to failure of healed specimens as a function of healing time and compare the kinetics of damage repair for *endo*- and *exo*-DCPD, and mixtures of the two isomers. Using catalyst loading levels previously reported to be effective for *endo*-DCPD, *exo*-DCPD was found to heal approximately 20 times faster than the *endo*-isomer, but with a lower healing efficiency. The fracture toughness of the repaired specimens decreased when the *exo* content of the blends was greater than 40% and, for the pure *exo*-DCPD, when the catalyst loadings were below 1%. Possible causes of the reduced healing efficiencies of the *exo*-DCPD healing agent are discussed.

Keywords: ring-opening metathesis polymerization; *endo*-dicyclopentadiene; *exo*-dicyclopentadiene; autonomic healing; self-healing

1. INTRODUCTION

A self-healing technology that uses the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) to repair the damage in polymer composites has recently been reported (White *et al.* 2001). In this autonomic healing system, DCPD is encapsulated in poly(urea–formaldehyde) microcapsules (Brown *et al.* 2003) that are subsequently dispersed in an Epon 828 epoxy matrix cured with diethylenetriamine (DETA). First-generation Grubbs' catalyst particles (Schwab *et al.* 1996) that have been incorporated into wax microspheres, for protection against DETA, are also embedded in the epoxy matrix (Rule *et al.* 2005). Upon fracture, DCPD is released from the ruptured microcapsules and is transported along the crack plane due to capillary action. The monomer dissolves the wax microspheres and the catalyst particles contained within. ROMP of the DCPD occurs, forming a thin polymer layer that adheres to and rebonds the crack planes.
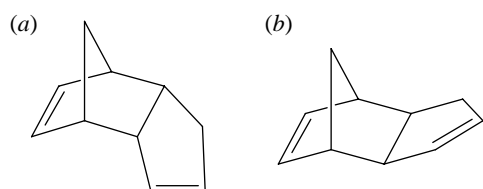
ROMP-based self-healing chemistry that were previously reported used the commercially available *endo*-stereoisomer of DCPD (figure 1*a*), owing to its long shelf life, ready availability and good mechanical properties of the resulting polymer. However, the *endo*-DCPD is known to have a slower polymerization rate than the *exo*-isomer (Larroche *et al.* 1984; Seehof

et al. 1993; Mathew *et al.* 1996; Ivin & Mol 1997; Wolfe & Wagener 1999; Fu & Seery 2001; Rule & Moore 2002), potentially limiting the kinetics of damage repair in self-healing. For many self-healing applications, it is desirable to have the fastest healing kinetics possible so long as the quality of the repair is not compromised. For *endo*-DCPD, Brown *et al.* (2002) found that at room temperature, approximately 25 min are required before any detectable recovery begins, and 10 h are required for the full recovery of mechanical toughness. This effect has been attributed to the healing agent's increasing degree of cure as a function of time (Brown *et al.* 2005). As the temperature is lowered, the time required for healing increases, and this effect, coupled with the relatively high melting point of *endo*-DCPD[1], limits the temperature window over which practical self-healing can occur (Liu *et al.* 2006). In stark contrast, *exo*-DCPD (figure 1*b*) has a gel time approximately 150 times faster than *endo*-DCPD, and the monomer itself does not solidify until temperatures below $-50°C$ (Smirnova *et al.* 1997). Thus, *exo*-DCPD may be a useful healing agent for low-temperature applications. Since self-healing is a complex problem that involves monomer transport, catalyst dissolution and transport, and polymerization, it is unclear how important faster reaction kinetics are to the overall rate and efficiency of healing.

---

*Author for correspondence (mauldin@lastate.edu).

One contribution of 9 to a themed supplement 'Self-healing polymers and composites'.

[1]The as-received commercially available *endo*-DCPD product used in this study has a depressed melting point of 15°C (Kessler & White 2002). Neat *endo*-DCPD has a melting point of 32.5°C.

Figure 1. Chemical structures of (*a*) *endo*- and (*b*) *exo*-DCPD.

In this study, *exo*-DCPD is incorporated into ROMP-based autonomic healing in an attempt to take advantage of these favourable kinetic properties. We also elucidate some of the problems that affect the healing efficiency when using fast healing agents and how to overcome these technical challenges.

2. METHODS

2.1. DCPD preparation

Endo-DCPD was received from Acros Organics and contained 95% purity DCPD, 2% being the *exo*-isomer. *Exo*-DCPD was prepared according to the procedures reported by Nelson & Kuo (1975) to a 85 : 15 ratio of *exo* : *endo* isomers. This blend is herein referred to as the *exo*-DCPD isomer. Both the stereoisomers were distilled and stabilized with 150 p.p.m. 4-*tert*-butylcatechol.

2.2. Gas chromatography

A Hewlett Packard 5890 Series II Gas Chromatograph with a 530 μm internal diameter capillary column and flame ionization detector was used to determine the *exo* : *endo* ratio of DCPD blends. The initial oven temperature was set to 80°C and the temperature was linearly ramped at a heating rate of $20°C \, min^{-1}$. Retention times for *exo*- and *endo*-DCPD were 1.89 and 1.95 min, respectively.

2.3. Microencapsulation

Both the isomers of DCPD were encapsulated in a urea–formaldehyde polymer shell via our previously reported method (Brown *et al.* 2003). *Exo*-DCPD contained 1 wt% dissolved polystyrene in order to adjust the liquid's viscosity to a value similar to *endo*-DCPD, which is ideal for the encapsulation procedure.

2.4. Catalyst and wax microsphere preparation

Grubbs' catalyst (bis(tricyclohexylphosphine)benzyli-dine ruthenium(IV) dichloride, Aldrich) was stored in an argon glovebox to prevent deactivation from air. The catalyst was prepared for healing by dissolving in N_2-sparged benzene ($50 \, mg \, ml^{-1}$), at which point the homogeneous solution was quenched in liquid nitrogen. The frozen benzene was then sublimed by placing the resulting solid under vacuum for 24 h (Jones *et al.* 2006). The resulting lyophilized catalyst was then encapsulated in wax by a previously established method (Rule *et al.* 2005) to give wax microspheres with 5 or 10 wt% of wax-protected Grubbs' catalyst.
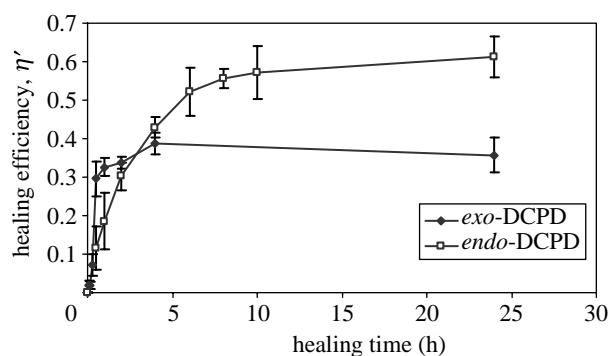

Figure 2. Progress of healing efficiency for *endo*- and *exo*-DCPD healing agents tested with self-activated protocols. An overall catalyst loading of 0.25 wt% was delivered via embedded wax microspheres (5 wt%) loaded with 5 wt% first-generation lyophilized Grubbs' catalyst.

2.5. Fracture testing

Fracture testing was performed on tapered double-cantilevered beam samples with an Epon 828/DETA matrix (Brown *et al.* 2002). Four samples were tested for each data point. Standard deviation of the data is indicated by error bars in the figures. The samples contained various loadings of embedded wax-protected catalyst, and DCPD was delivered either through the *in situ* protocol using 10 wt% $180 \pm 40 \, \mu m$ diameter microcapsules or the self-activated protocol with 10 μl injected manually along the crack plane. Specific details on sample preparation and fracture testing protocols used are reported by Brown *et al.* (2002). The strain energy (U) required to fail virgin and healed specimens was measured by calculating the total area under the load–displacement curves, and the healing efficiency was calculated as a simple ratio, $\eta' = U_{healed} / U_{virgin}$. In all the cases, both virgin and healed crack lengths were consistent and repeatable so that normalization by crack surface area (Rule *et al.* 2005) was not required.

Following the initial virgin fracture, tests were conducted at various elapsed healing times to determine the rate of fracture toughness recovery. All low-temperature test samples were stored in a cold room with a temperature range of 0–4°C for both 24 h prior to virgin fracture tests and during the entirety of the healing process. Fracture testing was performed at room temperature.

2.6. ESEM analysis

Fracture surfaces were prepared for analysis by sputter coating with gold–palladium. Microscopic images were taken with a Philips XL30 ESEM-FEG instrument.

3. RESULTS AND DISCUSSION

In previously reported self-healing studies, Brown *et al.* (2003) measured the kinetic progress of healing efficiency for *endo*-DCPD with 2.5 wt% loading of the catalyst by recording the fracture toughness values after varying periods of healing time, ranging from 10 min to 72 h. It has since been shown that with proper protection and dispersion, realized by encasing catalyst particles in wax (Rule *et al.* 2005), similar healing efficiencies can be
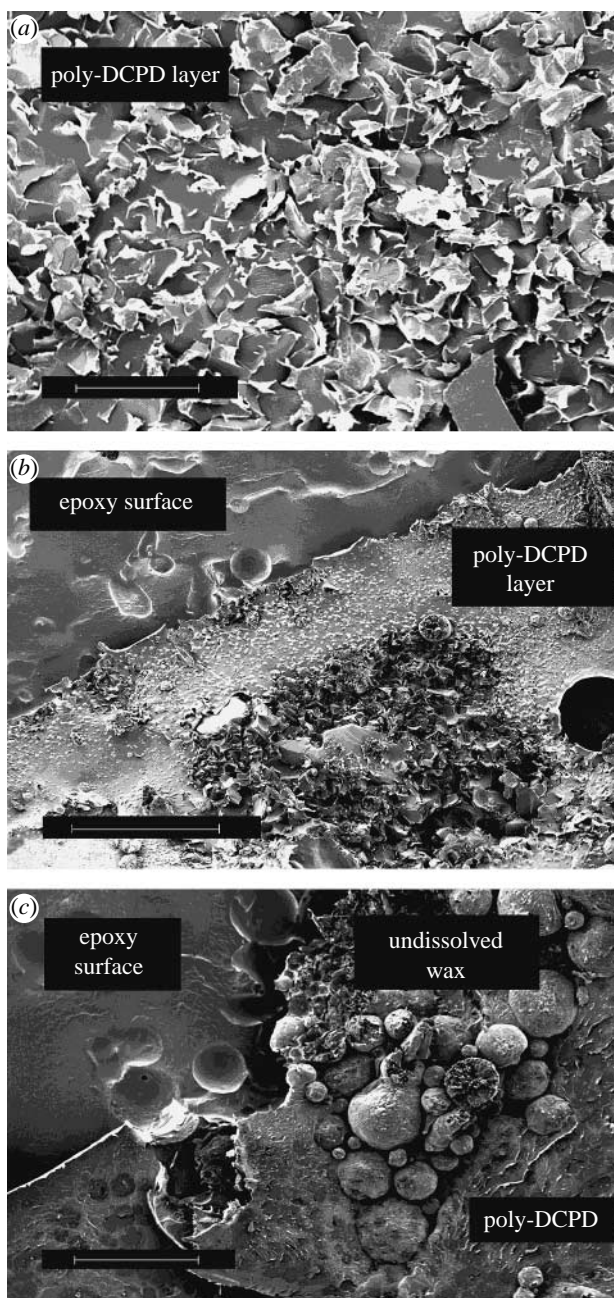
Figure 3. Representative ESEM images of TDCB epoxy matrix fracture planes for *endo-* and *exo-*DCPD healing agents. Images were taken on self-activated samples that were healed and subsequently fractured. Overall catalyst loading was 0.25 wt%, delivered by embedded wax microspheres (5 wt%) containing 5 wt% first-generation lyophilized Grubbs' catalyst: (*a*) *endo-*DCPD (scale bar, 200 µm), (*b*) *exo-*DCPD (scale bar, 500 µm) and (*c*) *exo-*DCPD (scale bar, 200 µm).

achieved with as little as 0.25 wt% catalyst loading. Owing to this performance enhancement, the wax-protected system was used in this study. For comparison purposes, *endo-*DCPD was re-evaluated using self-activated protocols and 0.25 wt% wax-protected catalyst. Comparable results were obtained compared to the original *endo-*DCPD system in which the catalyst was not protected (figure 2). For comparison of the two DCPD stereoisomers, identical tests were performed using *exo-*DCPD as a healing agent. *Exo-*DCPD cured too fast to measure the time at which the composite initially began recovering mechanical strength, but
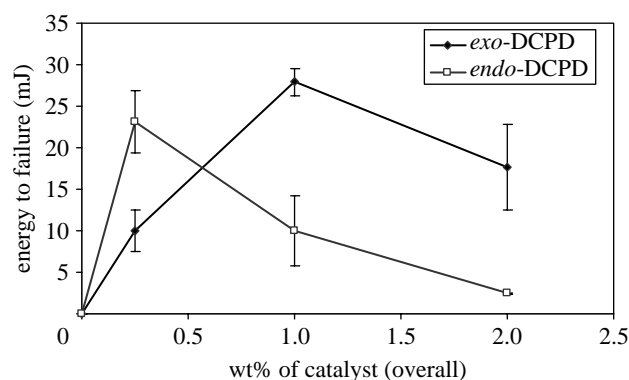

Figure 4. Effect of overall catalyst loading on energy required to fail samples healed with self-activated protocols. Catalyst was delivered via embedded wax microspheres (2.5, 10 or 20 wt%) loaded with 10 wt% first-generation lyophilized Grubbs' catalyst.
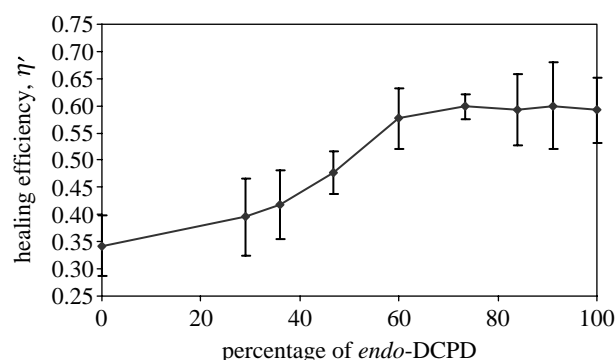

Figure 5. Effect of *exo/endo-*DCPD blends on healing efficiency for *in situ* healed samples containing an overall catalyst loading of 0.25 wt% delivered via embedded wax microspheres (5 wt%) containing 5 wt% first-generation lyophilized Grubbs' catalyst.

*exo-*DCPD was shown to reach a steady-state healing efficiency at approximately 30 min—roughly 20 times faster than the *endo-*DCPD (figure 2).

As shown in figure 2, the faster reaction kinetics of *exo-*DCPD has a detrimental effect on the healing efficiency. Healing via the *exo-*isomer leads to recovery of approximately 35% of the material's original fracture toughness—a value significantly less than that obtained via *endo-*DCPD. The ESEM images of self-activated fracture planes for the two isomers are presented in figure 3. For the *endo-*DCPD system (figure 3*a*), a continuous polymer layer covering a large percentage of the fracture plane is apparent. The flaky appearance of the poly-DCPD layer is indicative of cohesive failure of the polymerized healing and good load transfer across the crack plane. For the *exo-*DCPD system (figure 3*b*), a polymer film still forms on the crack plane, but the area of coverage is less and the film does not exhibit a flaky morphology consistently. Instead, patches of cohesively failed poly-DCPD localized around the catalyst particles and the sparseness of these patches on the fracture plane are probably the reasons for a decrease in healing efficiency. Further evidence that the root cause for poor healing in *exo-*DCPD is the incomplete dissolution of the wax-protected catalyst phase is shown in figure 3*c*. Jones *et al.* (2006) have shown a relationship between the
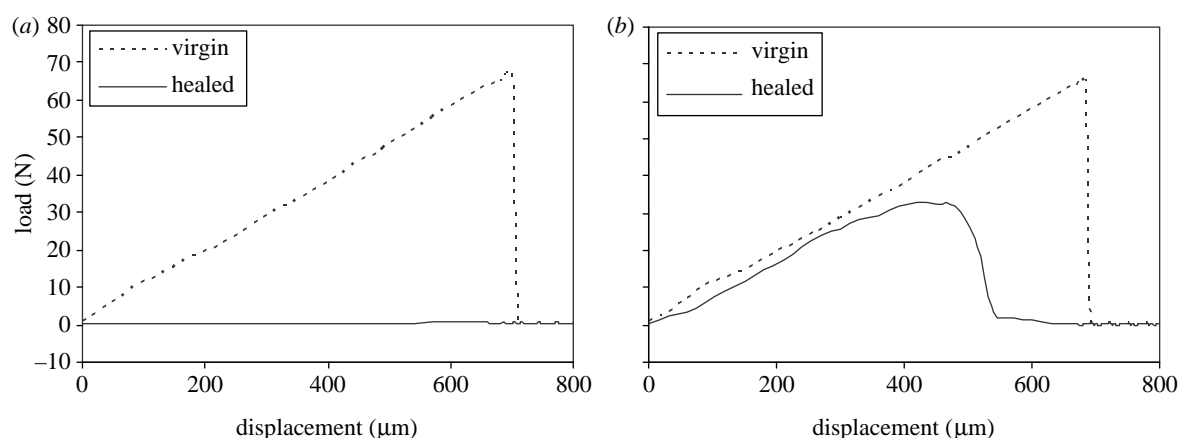
Figure 6. Load–displacement curves of virgin and *in situ* healed TDCB samples of (*a*) *endo*- and (*b*) *exo*-DCPD. Samples contained a catalyst loading of 0.25 wt% first-generation lyophilized Grubbs' catalyst delivered via embedded microcapsules (5 wt%) containing 5 wt% catalyst. Healing was carried out in a cold room (0–4°C) for 24 h.

fracture toughness recovery and the catalyst size, asserting that in order for *endo*-DCPD to approach maximum healing efficiency, the catalyst particles must be small enough to be fully dissolved prior to the onset of gelation. From the fracture plane images shown in figure 3, it appears that a similar phenomenon is occurring with *exo*-DCPD. Since *exo*-DCPD gels so quickly, the large wax particles are only partially dissolved by the monomer and the release of catalyst is incomplete. Jones *et al.* (2006) also showed that complete dissolution of lyophilized Grubbs' catalyst occurs in the range of 5–10 min. This dissolution rate is acceptable for self-healing with *endo*-DCPD, which gels in approximately 20 min at room temperature. But for *exo*-DCPD, which gels in seconds, much of the catalyst remains undissolved and a largely heterogeneous poly-DCPD film is formed on the crack plane.

In the tests described above, a 0.25% overall catalyst loading (5 wt% catalyst in wax and 5 wt% wax microspheres in the epoxy) was used because previous studies have shown this concentration to be the minimum necessary to achieve full healing with *endo*-DCPD healing agent (Rule *et al.* 2005), while increased catalyst concentrations were shown to only marginally affect healing efficiency (Brown *et al.* 2002). It is shown herein that *exo*-DCPD behaves differently, and increasing the catalyst concentration above 0.25 wt% leads to a significantly larger recovery of fracture toughness. The energy to failure data at higher catalyst loadings of self-activated samples are presented in figure 4. It is important to note that for these tests, wax microspheres containing 10 wt% Grubbs' catalyst were used in order to reduce the total amount of wax in the system[2].

As shown in figure 4, when the catalyst concentration is increased from 0.25 to 1 wt%, the performance of the *exo*-DCPD system is greatly enhanced and slightly exceeds the maximum results obtained for the *endo*-DCPD (at 0.25 wt%). This enhancement in performance lends support to the hypothesis that *exo*-DCPD's lower healing efficiency is due to insufficient time for catalyst dissolution. As the catalyst concentration increases, enough catalyst is dissolved to allow *exo*-DCPD to polymerize more completely.

In order to achieve high healing efficiency coupled with fast kinetics at the more practical catalyst loading of 0.25 wt%, we investigated the healing agent blends of the two isomers. By adding increasing amounts of *endo*-DCPD to *exo*-DCPD, the gelation time of the resulting blend can be tuned so that an appropriate amount of catalyst is dissolved before gelation occurs. Healing efficiency of *in situ* healed samples for a series of healing agent blends of the two isomers using a catalyst loading of 0.25 wt% (5 wt% catalyst in wax and 5 wt % wax-protected catalyst in epoxy matrix) are presented in figure 5. Healing performance increases with increasing *endo* content until a blend of 60 : 40 *endo* : *exo*-DCPD is reached, at which point the healing efficiency is effectively constant. This demarcation of the critical blend ratio (60 : 40 *endo* : *exo*) probably coincides with an effective polymerization rate that is just slow enough to allow full dissolution of the catalyst and healing of the matrix is maximum.

As a means to further exploit the faster healing kinetics of *exo*-DCPD, we briefly examined its ability to heal at sub-ambient temperatures. Figure 6 shows the virgin and healed fracture test results of the *exo*- and *endo*-isomer of DCPD healed in a cold room with a temperature range of 0–4°C. From the complete lack of healing for *endo*-DCPD shown in figure 6*a*, we suspect that solidification of the monomer due to freezing limits *endo*-DCPD's low-temperature healing capabilities. *Endo*-DCPD doped with melting point-depressing impurities, already present in the as-received commercial product, is known to freeze at 15°C (Kessler & White 2002), so that within the cold room environment (0–4°C), the encapsulated healing agent solidified. *Exo*-

---

[2] For both isomers of DCPD, a trend of sharply decreased healing performance is seen if the concentration of encasing wax microspheres is increased too high. In the original study of encasing Grubbs' catalyst in wax, Rule *et al.* (2005) experienced a similar trend in healing efficiency attributed to dissolved wax in the poly-DCPD, plasticizing the healing agent and reducing its strength. Brown *et al.* (2002) did not experience this problem in their study with unprotected catalyst. Since the overall loading of wax was increased in our study as the catalyst concentration increased, this sharp decrease in healing is attributed to plasticization of poly-DCPD by the wax. Presumably, *endo*-DCPD begins this sharp decrease at lower concentrations than *exo*-DCPD because its longer gelation time allows more wax to dissolve into the monomer.

DCPD, which freezes at temperatures below $-50°C$, showed no degradation in healing capability at this temperature range (figure 6*b*) and the load–displacement curves similar to those at ambient temperatures were observed (data not shown).

4. CONCLUSION

The *exo*-stereoisomer of DCPD was shown to have self-healing kinetics superior to the *endo*-isomer, consistent with its faster polymerization kinetics. However, the decreased gelation time of *exo*-DCPD does not allow sufficient time to dissolve the wax and/or a sufficient quantity of the embedded catalyst. Consequently, the faster-healing *exo*-DCPD shows decreased healing efficiency when compared with the *endo*-DCPD at 0.25 wt% catalyst loading. However, the combination of fast kinetics and high healing efficiency was demonstrated by appropriate blending of *exo/endo*-DCPD healing agents and by adjusting catalyst loadings to optimal levels. By using healing agents with short gel times such as *exo*-DCPD, healing time can be fast enough to repair the damage shortly after cracks appear. Healing agents with fast kinetics can also extend the temperature range over which the healing can take place, as was demonstrated for *exo*-DCPD at 0°C. Faster healing kinetics may also be important for arresting the fatigue damage under extreme conditions by quickly healing rapidly propagating cracks.

REFERENCES

Brown, E. N., Sottos, N. R. & White, S. R. 2002 Fracture testing of a self-healing polymer composite. *Exp. Mech.* **42**, 372–379. (doi:10.1007/BF02412141)

Brown, E. N., Kessler, M. R., Sottos, N. R. & White, S. R. 2003 *In-situ* poly(urea-formaldehyde) microencapsulation of dicyclopentadiene. *J. Microencapsulation* **20**, 719–730. (doi:10.1080/0265204031000154160)

Brown, E. N., White, S. R. & Sottos, N. R. 2005 Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part II: *in situ* self-healing. *Compos. Sci. Technol.* **65**, 2474–2480. (doi:10.1016/j.compscitech. 2005.04.053)

Fu, Q. & Seery, T. A. P. 2001 The study of ring opening metathesis polymerization kinetics for endo and exo norbornene derivative monomer with *in-situ* 1H-NMR technique. *Polym. Prep.* **42**, 341–342.

Ivin, K. J. & Mol, J. C. 1997 *Olefin metathesis and metathesis polymerization*. San Diego, CA: Academic Press.

Jones, A. S., Rule, J. D., Moore, J. S., White, S. R. & Sottos, N. R. 2006 Catalyst morphology and dissolution kinetics of self-healing polymers. *Chem. Mater.* **18**, 1312–1317. (doi:10.1021/cm051864s)

Kessler, M. R. & White, S. R. 2002 Cure kinetics of the ring-opening metathesis polymerisation of dicyclopentadiene. *J. Polym. Sci. A* **40**, 2373–2383. (doi:10.1002/pola.10317)

Larroche, C., Laval, J. P., Lattes, A. & Basset, J. M. 1984 Ring opening polymerization of norbornene substituted with amine and ammonium groups. *J. Org. Chem.* **49**, 1886–1890. (doi:10.1021/jo00185a008)

Liu, X., Lee, J. K., Yoon, S. H. & Kessler, M. R. 2006 Characterization of diene monomers as healing agents for autonomic damage repair. *J. Appl. Polym. Sci.* **101**, 1266–1272. (doi:10.1002/app.23245)

Mathew, J. P., Reinmuth, A., Melia, J., Swords, N. & Risse, W. 1996 (η3-Allyl)palladium(II) and palladium (II) nitrile catalysts for the addition polymerization of norbornene derivatives with functional groups. *Macromolecules* **29**, 2755–2763. (doi:10.1021/ma9515285)

Nelson, G. L. & Kuo, C.-L. 1975 An improved procedure for the preparation of exo-dicyclopentadiene. *Synthesis* **105**, 105–106. (doi:10.1055/s-1975-23674)

Rule, J. D. & Moore, J. S. 2002 ROMP reactivity of endo- and exo-dicyclopentadiene. *Macromolecules* **35**, 7878–7882. (doi:10.1021/ma0209489)

Rule, J. D., Brown, E. N., Sottos, N. R., White, S. R. & Moore, J. S. 2005 Wax-protected catalyst microspheres for efficient self-healing materials. *Adv. Mater.* **17**, 205–208. (doi:10.1002/adma.200400607)

Schwab, P., Grubbs, R. H. & Ziller, J. W. 1996 Synthesis and applications of RuCl2(:CHR′)(PR3)2: The influence of the alkylidene moiety on metathesis activity. *J. Am. Chem. Soc.* **118**, 100–110. (doi:10.1021/ja952676d)

Seehof, N., Grutke, S. & Risse, W. 1993 Selective reaction with exo isomers in ring-opening olefin metathesis polymerization (ROMP) of fluoroalkyl-substituted norbornene derivatives. *Macromolecules* **26**, 695–700. (doi:10.1021/ma00056a021)

Smirnova, N. N., Lebedev, B. V., Kiparisova, E. G., Makovetskii, K. L. & Ostrovskaya, I. Y. 1997 Thermodynamics of endo and exo-dicyclopentadienes, their metathesis and addition polymerizations, and the resulting polymers. *Polym. Sci. USSR* **39**, 1323–1331.

White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N. & Viswanathan, S. 2001 Autonomic healing of polymer composites. *Nature* **409**, 794–797. (doi:10.1038/35057232)

Wolfe, P. S. & Wagener, K. B. 1999 Investigation of organoboronates in metathesis polymerization. *Macromolecules* **32**, 7961–7967. (doi:10.1021/ma981784s)