Self-healing kinetics and the stereoisomers of dicyclopentadiene

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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 1a), 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, limits the temperature window over which practical self-healing can occur (Liu et al. 2006). In stark contrast, exo-DCPD (figure 1b) 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.

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¹The as-received commercially available endo-DCPD product used in this study has a depressed melting point of 13°C (Kessler & White 2002). Neat endo-DCPD has a melting point of 32.5°C.
temperature was set to 80
exo
flame ionization detector was used to determine the
distilled and stabilized with 150 p.p.m. 4-
butylcatechol.
linearly ramped at a heating rate of 20
The catalyst was prepared for healing by dissolving in
an argon glovebox to prevent deactivation from air.
Grubbs’ catalyst (bis(tricyclohexylphosphine)benzyli-
2.4. Catalyst and wax microsphere preparation
DCPD, which is ideal for the encapsulation procedure.
adjust the liquid’s viscosity to a value similar to
contained 1 wt% dissolved polystyrene in order to
Both the isomers were distilled and stabilized with 150 p.p.m. 4-tert-
2.2. Gas chromatography
A Hewlett Packard 5890 Series II Gas Chromatograph
with a 530 \( \mu \)m 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)benzylidine
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 1. Chemical structures of (a) endo- and (b) exo-DCPD.](image)

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

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-
cantilever 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 ± 40 \( \mu \)m diameter
microparticles or the self-activated protocol with 10 \( \mu \)l
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, \( \eta = \frac{U_{\text{healed}}}{U_{\text{virgin}}} \). In
all the cases, both virgin and healed crack lengths were
consistent and repeatable so that normalization by
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
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 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 3a), 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 3b), 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 3c. Jones et al. (2006) have shown a relationship between the...
fracture toughness recovery and the catalyst size, asserting that in order for \textit{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 \textit{exo}-DCPD. Since \textit{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 \textit{endo}-DCPD, which gels in approximately 20 min at room temperature. But for \textit{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 \textit{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 \textit{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.

As shown in figure 4, when the catalyst concentration is increased from 0.25 to 1 wt%, the performance of the \textit{exo}-DCPD system is greatly enhanced and slightly exceeds the maximum results obtained for the \textit{endo}-DCPD (at 0.25 wt%). This enhancement in performance lends support to the hypothesis that \textit{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 \textit{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 \textit{endo}-DCPD to \textit{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 \textit{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 \textit{endo} content until a blend of 60 : 40 \textit{endo} : \textit{exo}-DCPD is reached, at which point the healing efficiency is effectively constant. This demarcation of the critical blend ratio (60 : 40 \textit{endo} : \textit{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 \textit{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 \textit{exo}- and \textit{endo}-isomer of DCPD healed in a cold room with a temperature range of 0–4°C. From the complete lack of healing for \textit{endo}-DCPD shown in figure 6a, we suspect that solidification of the monomer due to freezing limits \textit{endo}-DCPD’s low-temperature healing capabilities. \textit{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. 

\textit{Exo}-DCPD, on the other hand, is known to freeze at 15°C, but solidification of the monomer is less likely, especially at room temperature (8°C).

Figure 6. Load–displacement curves of virgin and \textit{in situ} healed TDCB samples of (a) \textit{endo}- and (b) \textit{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.

3For both isomers of DCPD, a trend of sharply decreased healing performance is seen if the concentration of 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, \textit{endo}-DCPD begins this sharp decrease at lower concentrations than \textit{exo}-DCPD because its longer gelation time allows more wax to dissolve into the monomer.
DCPD, which freezes at temperatures below $-50^\circ$C, showed no degradation in healing capability at this temperature range (figure 6b) 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.

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