

Life extension of self-healing polymers with rapidly growing fatigue cracks

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Self-healing polymers, based on microencapsulated dicyclopentadiene and Grubbs' catalyst embedded in the polymer matrix, are 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. The amount of fatigue-life extension depends on the relative magnitude of the mechanical kinetics of crack propagation and the chemical kinetics of healing. As the healing kinetics are accelerated, greater fatigue life extension is achieved. The use of wax-protected, recrystallized Grubbs' catalyst leads to a fourfold increase in the rate of polymerization of bulk dicyclopentadiene and extends the fatigue life of a polymer specimen over 30 times longer than a comparable non-healing specimen. The fatigue life of polymers under extremely fast fatigue crack growth can be extended through the incorporation of periodic rest periods, effectively training the self-healing polymeric material to achieve higher endurance limits.

Keywords: autonomic materials; self-healing polymers; fatigue

1. INTRODUCTION

Fatigue and the associated slow accumulation of damage and deterioration in performance plague all materials, particularly those that fail in a brittle manner. Inspired by biological systems that continuously adapt and remodel in response to continuous (or periodic) fatigue cycles, the self-healing polymer reported here responds to fatigue loading by autonomic processes that lead to higher endurance limits and life extension, or even complete arrest of crack growth (infinite life).

The materials system consists of a self-healing polymer that incorporates a microencapsulated healing agent (dicyclopentadiene) and bis-tricyclohexylphosphine benzylidene ruthenium (IV) dichloride, a solid chemical catalyst known as Grubbs' catalyst, in a polymer matrix (EPON 828, Miller-Stephenson Chemical Co.; White *et al.* 2001; Brown *et al.* 2002). As shown in figure 1, a crack is formed in the polymer and then grown under cyclic loading in tension. Embedded microcapsules are ruptured by this crack growth, which then release the dicyclopentadiene into the crack plane through capillary action. Polymerization of the dicyclopentadiene is triggered by contact with the suspended catalyst phase. As the

healing reaction progresses, the crack plane fills with polymerized dicyclopentadiene and provides a crack-tip shielding effect (Elber 1970; Ur-Rehman & Thomason 1993; Brown *et al.* 2005*a,b*) leading to the retardation or permanent arrest of further fatigue crack propagation.

Brown *et al.* (2002) have demonstrated that this materials system recovers up to 90% of its original fracture toughness after a quasi-static Mode I fracture. A pin-loaded, tapered double-cantilever-beam specimen was subjected to a constant displacement rate of $5 \mu\text{m s}^{-1}$ until unstable crack growth occurred. After fracture, the polymer halves were placed back together and allowed to rest at room temperature for 48 h. Subsequent testing of the same specimen resulted in a 90% recovery of the original fracture toughness. In addition, the inclusion of the self-healing materials (microcapsules and catalyst) in the polymer matrix significantly increased the inherent fracture toughness of the virgin polymer specimen (Brown *et al.* 2004). The quasi-static fracture of a neat polymer specimen resulted in a predominantly mirror-like smooth fracture surface typical of cleavage-like brittle fracture. On the other hand, the quasi-static fracture of the self-healing system resulted in fracture surfaces that are predominantly covered with hackle markings (a surface morphology resulting from small-scale secondary crack formation parallel to the fracture plane; Rabinovith *et al.* 2000), which leads to increased fracture toughness.

Most polymeric materials suffer from poor fatigue resistance and will fail at stress levels much lower than they can withstand under monotonic loading conditions

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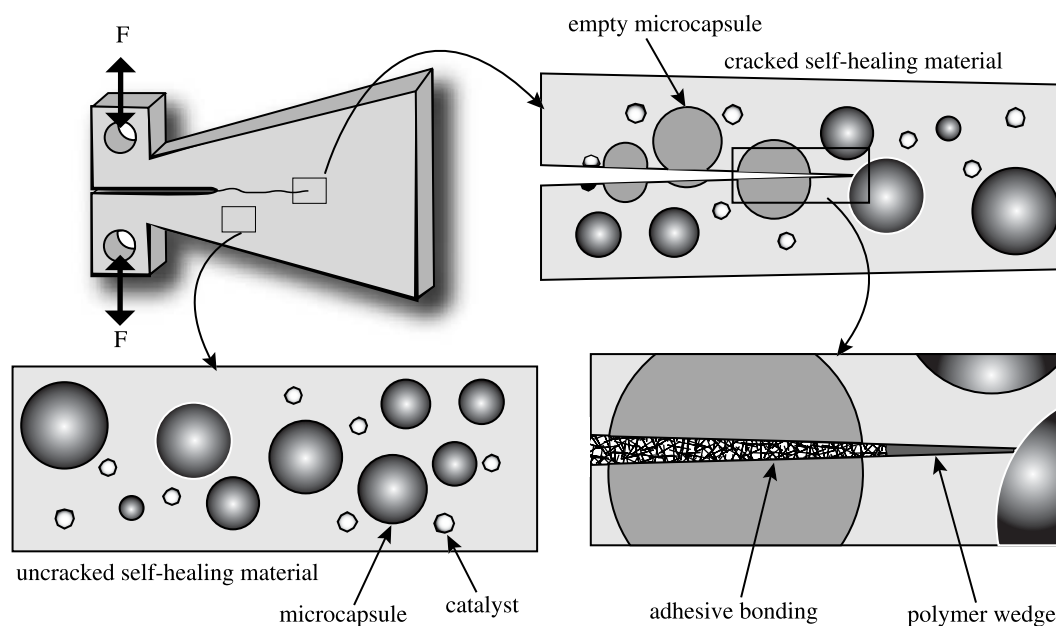


Figure 1. Details of the self-healing process during fatigue.

(Sauer & Richardson 1980). This behaviour leads to fatigue crack propagation at relatively low stress levels and represents a critical failure mode in polymers (Sutton 1974). One method of improving the fatigue performance of brittle polymeric materials is to increase the inherent fracture toughness of the polymer. Methods of increasing the fracture toughness of the polymer include incorporating a rubbery second phase (Bascom *et al.* 1981; Kinloch *et al.* 1983; Becu *et al.* 1997; Rey *et al.* 1999; Hayes & Seferis 2001; Nobelen *et al.* 2003), incorporating solid particles (Azimi *et al.* 1995; Sautereau *et al.* 1995; McMurray & Amagi 1999) or the addition of microcapsules (Azimi *et al.* 1996; Brown *et al.* 2006) to the polymer matrix. Additional methods of reducing the fatigue crack propagation rate include crack-tip shielding mechanisms such as crack closure (Elber 1970, 1971; Ur-Rehman & Thomason 1993; Sharp *et al.* 1997; Shin *et al.* 1998; Song *et al.* 1998), which introduces a wedge in the crack plane and reduces the effective stress intensity at the crack tip, and hydrodynamic pressure crack-tip shielding (experiments and theory developed mainly for metals), which reduces fatigue crack growth due to the viscous flow between the crack faces (Galvin & Naylor 1965; Endo *et al.* 1972; Polk *et al.* 1975; Plumbridge 1977; Plumbridge *et al.* 1985; Tzou *et al.* 1985*a,b*; Davis & Ellison 1989; Yi *et al.* 1999; Brown *et al.* 2005*a*).

Self-healing polymers based on microencapsulated healing agents benefit from all of the mechanisms listed previously for improving fatigue performance. The fracture toughness of the polymer is increased by the addition of the microcapsules (Brown *et al.* 2006) and once a microcapsule is fractured, release of the healing agent into the crack plane initiates hydrodynamic crack-tip shielding. After the liquid dicyclopentadiene contacts an exposed catalyst particle, polymerization takes place and the viscosity of the dicyclopentadiene increases until a solid wedge of polydicyclopentadiene is formed in the crack plane. Brown *et al.* (2005*b*) showed that the fatigue performance of self-healing polymers

with 20 wt% of dicyclopentadiene-filled microcapsules and 2.5 wt% of catalyst depends on the fatigue stress intensity range (ΔK). At low stress intensity ranges (slow mechanical kinetics of crack growth), the fatigue crack is arrested, while at high stress intensity ranges (fast mechanical kinetics of crack growth), the fatigue crack is unaffected by the self-healing system unless a rest period is incorporated during the fatigue loading. Even with a rest period, only a moderate life extension was obtained.

The effectiveness of the healing system after a fracture event depends on the amount of time the specimen has been allowed to heal (Brown *et al.* 2002; i.e. the duration of polymerization of the dicyclopentadiene). During fatigue loading, the mechanical damage is continuously accumulating while, simultaneously, healing takes place. Improved healing and faster chemical kinetics are needed for further enhancement of the fatigue crack resistance of polymers. One obvious method of accelerating the healing kinetics is to use faster curing healing agents. Converting *endo*-dicyclopentadiene isomer into *exo*-dicyclopentadiene results in significantly faster polymerization of the monomer (Rule & Moore 2002). Using faster reacting monomers such as 5-ethylidene-2-norbornene, or blends of different monomers (Liu *et al.* 2006), can result in extremely fast polymerization of the healing agent. In addition to modifying the healing agent, greater concentrations of catalyst dissolved into the dicyclopentadiene result in faster curing times (Kessler & White 2002).

Rule *et al.* (2005) have shown that encapsulating the catalyst in wax microspheres can prevent deactivation of the catalyst by the amine-based epoxy curing agents used in self-healing epoxies and dramatically improve the dispersion of the catalyst throughout the polymer matrix. Less catalyst is needed for effective healing since it is more reactive and more uniformly dispersed. Jones *et al.* (2006) have shown that for more rapid healing not only does the kinetics of polymerization

need to be accelerated, but also the dissolution kinetics of the catalyst. If the polymerization kinetics of the healing agent is rapid, while the catalyst dissolution is slow, the catalyst may not have a chance to fully dissolve into the healing agent. In this case, healing is heterogeneous and isolated in locations around catalyst particles, leaving the majority of the fracture plane unhealed and dramatically reducing the healing efficiency of the system.

Self-healing polymers based on embedded microcapsules of dicyclopentadiene and catalyst in a polymer matrix have been demonstrated (Brown *et al.* 2005*b*) to be effective in preventing fatigue crack growth under conditions of slow mechanical kinetics and retarding crack growth under moderate conditions. Improvements to the chemical kinetics of healing or incorporating prescribed rest periods need to be used to effectively prevent fatigue crack growth under higher stress intensity ranges (fast mechanical kinetics). In the current work, the role of accelerated chemical kinetics via catalyst tailoring, as well as periodic rest periods, on the fatigue response of self-healing polymers is investigated.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and specimen fabrication

Dicyclopentadiene-filled, urea-formaldehyde microcapsules were fabricated by *in situ* polymerization in an oil-in-water emulsion. Details of the microencapsulation process can be found in Brown *et al.* (2003). Wax microspheres containing Grubbs' catalyst were fabricated by rapidly stirring a 70°C aqueous solution of melted wax, catalyst and poly(ethylene-co-maleic anhydride) with an overhead digital mixer. Cold water was added to the solution to solidify the wax. The wax microspheres were then filtered, dried and sifted before use. Wax microspheres excluding catalyst were fabricated in an identical fashion.

Different morphologies of Grubbs' catalyst were used in this study. The as-received catalyst (Sigma-Aldrich) consisted of large (approx. 150 µm long by 40 × 50 µm in cross-section) parallelepiped crystals. The other morphologies, achieved by recrystallizing by non-solvent addition and freeze-drying the as-received catalyst, consisted of a rod-like morphology (5 µm in diameter and up to 200 µm long) and a platelet morphology (1 µm thick and 5 µm in diameter). Details of the recrystallization processes can be found in Jones *et al.* (2006). Scanning electron microscope images of different catalyst morphologies are shown in figure 2.

Self-healing, tapered, double-cantilever-beam (TDCB) specimens (Mostovoy *et al.* 1967) were fabricated using a two-step moulding process resulting in a sample geometry shown in figure 3. First, a neat polymer shell with a void at the core was fabricated by pouring degassed EPON 828 epoxy resin (DGEBA) and 12 parts per hundred (pph) Ancamine DETA (diethylenetriamine) curing agent into a mould with an appropriate insert and allowing it to cure for 24 h at 30°C. The insert was removed and the core was subsequently filled with a degassed mixture of epoxy,

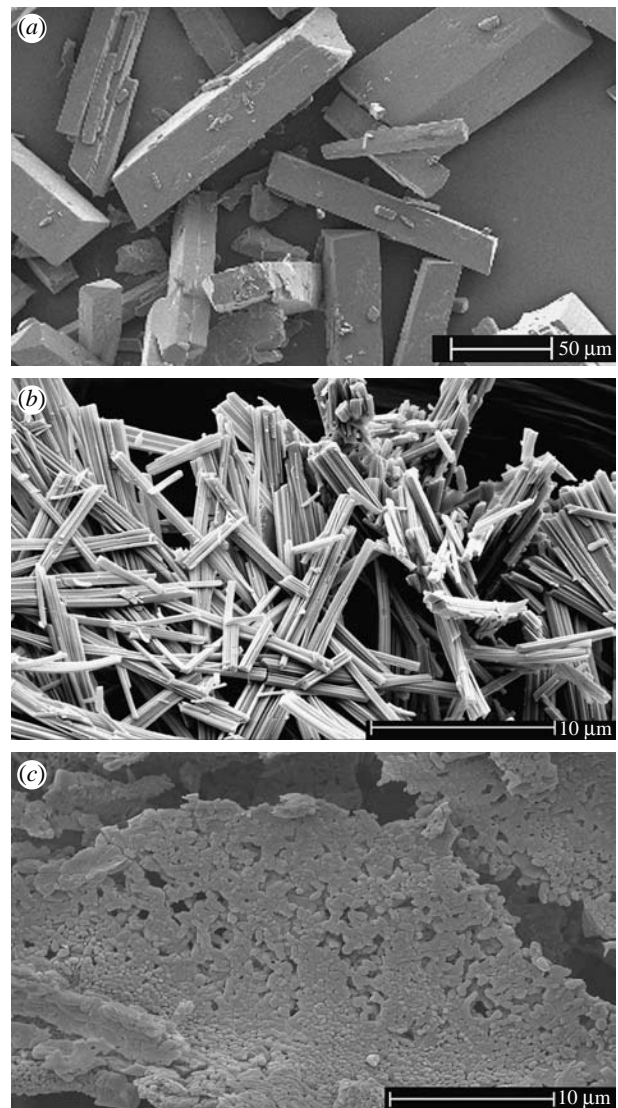


Figure 2. Morphologies of Grubbs' catalyst: (a) as-received, (b) recrystallized by non-solvent addition and (c) recrystallized by freeze-drying.

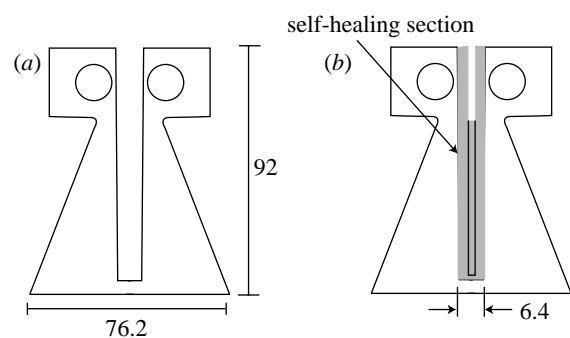


Figure 3. Geometries during the moulding process: (a) polymer shell and (b) complete specimen (grey area indicates the self-healing polymer material), dimensions in millimetre.

DETA and the self-healing constituents. The specimen was then allowed to cure for 24 h at room temperature followed by a 24 h cure at 30°C. In all cases (where that component is used and except as noted), the quantity of each component was as follows: 20 pph of 180 µm diameter dicyclopentadiene-filled microcapsules; 5 pph of wax microspheres; and 5 pph of wax microspheres

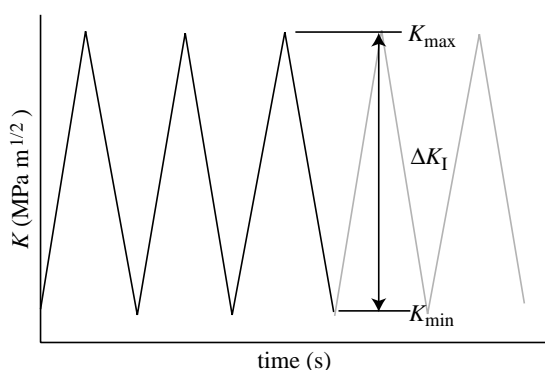


Figure 4. Schematic of fatigue loading parameters, frequency is 5 Hz, $R=0.1$.

containing 5 wt% Grubbs' catalyst. This process created TDCB specimens with self-healing components along the path of the crack and neat epoxy material everywhere else. All polymer control specimens were created in an identical manner (initially creating the epoxy shell, then filling the core with neat epoxy, etc.) to ensure that any residual stresses due to the two-step fabrication process would be identical in all cases.

2.2. Experimental processes

Fatigue fracture testing was performed by pre-cracking the TDCB specimens with a razor blade and immediately cyclically loading the specimen under load-control conditions on an Instron DynoMight 8841 low-load frame with a 250 N load cell. The specimen was pin-loaded and a 5 Hz triangular waveform was applied with a stress ratio (R) of 0.1 and a maximum stress intensity of $0.676 \text{ MPa m}^{1/2}$, as shown in figure 4. Mode I fatigue cracks were constrained along the centreline of the specimen by use of side grooves moulded in the specimen. The crack tip was measured optically in four to five locations along the length of the specimen during the experiment. Due to the taper on the double-cantilever-beam specimen, there is a linear relationship between the compliance of the specimen and the crack length. During the course of the experiment, the crack-tip position was determined from the specimen compliance along with optical measurements.

The performance of a self-healing system under fatigue crack growth was evaluated using the fatigue life extension ratio (λ). This ratio was defined as the difference between the number of cycles to failure of a self-healing specimen (N_{healed}) versus the number of cycles to failure of a control (without healing) specimen (N_{control}), as shown in equation (2.1),

$$\lambda = \frac{N_{\text{healed}} - N_{\text{control}}}{N_{\text{control}}} \quad (2.1)$$

The gel time measurements were made by placing either the recrystallized catalyst or the as-received catalyst (3 mg) into three 4 ml glass vials and adding 1.0 ml of *endo*-dicyclopentadiene to the vial via syringe. Each vial was shaken for 1 min and was periodically observed and shaken. The gel time was recorded when the monomer solution stopped flowing as the vial was rotated.

3. RESULTS AND DISCUSSION

3.1. Effect of catalyst morphology and wax protection

Recrystallized catalyst dissolves into dicyclopentadiene faster than the as-received catalyst (Jones *et al.* 2006) and accelerates the overall polymerization kinetics. Figure 5 shows the gel times for the polymerization of dicyclopentadiene using different concentrations of as-received and recrystallized catalyst. The recrystallized catalyst gels the dicyclopentadiene approximately four times faster than the as-received catalyst. Unfortunately, the faster dissolving morphology is also more susceptible to deactivation resulting from the exposure to amine-based epoxy curing agents. Therefore, wax encapsulation of the recrystallized catalyst is needed to prevent significant deactivation of the catalyst during the fabrication of the polymer specimen. The improved reactivity and dispersion of the protected catalyst allows a significant reduction in the amount required to create effective self-healing polymers. Retardation of fatigue crack growth can be accomplished with catalyst ratios as low as 0.25 pph versus previous (Brown *et al.* 2005*b*) catalyst loadings of 2.5 pph.

The fatigue performance of three self-healing materials systems and two control specimens is compared in figure 6. The fatigue response of a polymer specimen without any healing constituents (curve A) serves as a baseline control. As a second control, fatigue data for a specimen that contains dicyclopentadiene-filled microcapsules but no catalyst (curve B) is included in figure 6. The improvement in fatigue life for control sample B with respect to A is due to the toughening effect of the microcapsules and the hydrodynamic crack-tip shielding after the release of the dicyclopentadiene into the crack plane. The third curve (C) is from a self-healing specimen that comprised a wax-protected, as-received catalyst along with microcapsules of dicyclopentadiene. The chemical kinetics of healing are relatively slow due to the low catalyst dissolution rate and, consequently, low concentration of the catalyst in the dicyclopentadiene.

Curve D in figure 6 corresponds to a self-healing materials system that comprised dicyclopentadiene microcapsules and recrystallized catalyst in wax microspheres. Here, the faster dissolving catalyst is protected from deactivation by the wax and results in faster healing kinetics, and thus greater life extension. Experiments on the quickly dissolving catalyst morphology formed by freeze-drying the as-received catalyst (curve E) show even greater fatigue life extension. In comparison with other materials systems, more significant retardation of crack growth is achieved earlier in the test due to faster healing kinetics. The non-uniformity of the crack growth curve correlates to local variations in the availability of catalyst on the fracture plane. A careful examination of the fatigue fracture surfaces as shown in figure 7 reveals that in regions of the crack plane where there is reduced catalyst concentration (due to the non-uniform dispersion of the catalyst), the crack growth rate is accelerated, and in areas where there is high catalyst concentration, the surface is covered with poly-DCPD,

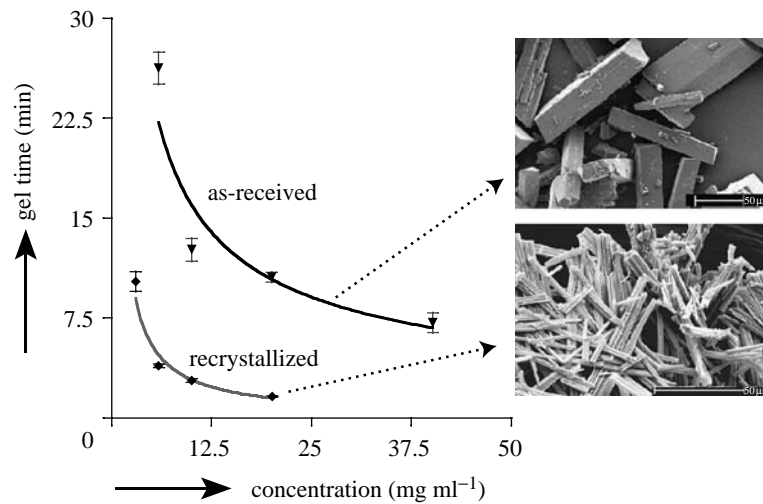


Figure 5. Gel time of DCPD with different concentrations of as-received catalyst and recrystallized Grubbs' catalyst by non-solvent addition.

the crack growth is retarded and, in some regions, practically arrested.

The inclusion of wax microspheres into the polymer matrix influences the fatigue performance of the polymer significantly. The wax not only acts as an additional toughening component, but also dissolves into the released dicyclopentadiene leading to increased viscosity of the fluid and additional hydrodynamic crack-tip shielding. Figure 8 summarizes the effect of adding wax on the fatigue life of materials systems that contain microcapsules of dicyclopentadiene. The specimen corresponding to curve F does not include the catalyst; hence, even though no chemical healing takes place, the addition of wax alone increases the fatigue life. Figure 8 also contains data for a self-healing specimen (curve G) that includes recrystallized catalyst without wax microspheres. This specimen was fabricated using 2.5 pph of catalyst for comparison with the prior study by Brown *et al.* (2005b) (10 times the amount used in all other specimens). In this case, the faster polymerization kinetics of the recrystallized catalyst results in longer fatigue life, but due to the catalyst being exposed to the amine-based curing agents of the epoxy during the specimen fabrication, its reactivity is significantly reduced.

Table 1 summarizes the fatigue life extension factors (equation (2.1)) for all the specimens presented in figures 6 and 8. The life extension factor has been calculated with respect to both a neat polymer specimen to demonstrate the total effect of the self-healing constituents and the microcapsule-only specimen to demonstrate how self-healing polymers would perform compared with other non-healing toughening mechanisms. At the relatively high loading rate for these experiments, the greatest life extension was achieved for the specimen with the fastest polymerization kinetics.

3.2. Interplay between mechanical and chemical kinetics

The mechanical kinetics of fatigue crack growth is dependent on the stress ratio ($R = K_{\min}/K_{\max}$), the

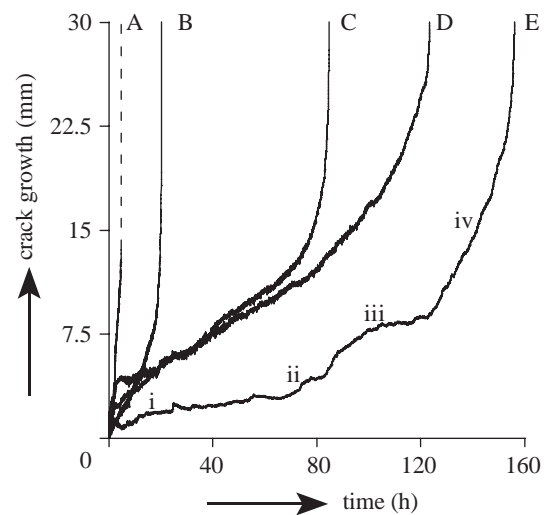


Figure 6. Fatigue at $K_{\max} = 0.676 \text{ MPa m}^{1/2}$, $R = 0.1$, $f = 5 \text{ Hz}$ of TDCB polymer specimens. A, neat polymer; B, contains 20 pph microcapsules; C, contains 20 pph microcapsules and 5 pph of wax microspheres with 5 wt% of as-received catalyst; D, contains 20 pph microcapsules and 5 pph of wax microspheres with 5 wt% of recrystallized catalyst (non-solvent addition); E, contains 20 pph microcapsules and 5 pph of wax microspheres with 5 wt% of recrystallized catalyst (freeze dried). Numerals i, ii, iii and iv on curve E demarcate the locations where SEM images of the fracture plane are provided in figure 7.

frequency (f) and the maximum applied stress intensity factor (K_{\max}). Keeping R and f constant, the mechanical kinetics is controlled through K_{\max} . As K_{\max} is increased, the crack growth rate (da/dN) will increase according to the Paris power law,

$$\frac{da}{dN} = C(K_{\max} - K_{\min})^n. \quad (3.1)$$

There is a limit, however, as K_{\max} approaches the quasi-static fracture toughness of the polymer, K_{IC} , unstable fracture will occur. Data in figures 6 and 8 correspond to a K_{\max} of $0.676 \text{ MPa m}^{1/2}$, which is 62% of the quasi-static fracture toughness, $K_{\max}/K_{IC} = 0.62$. This ratio is significantly higher than the range of stress intensities

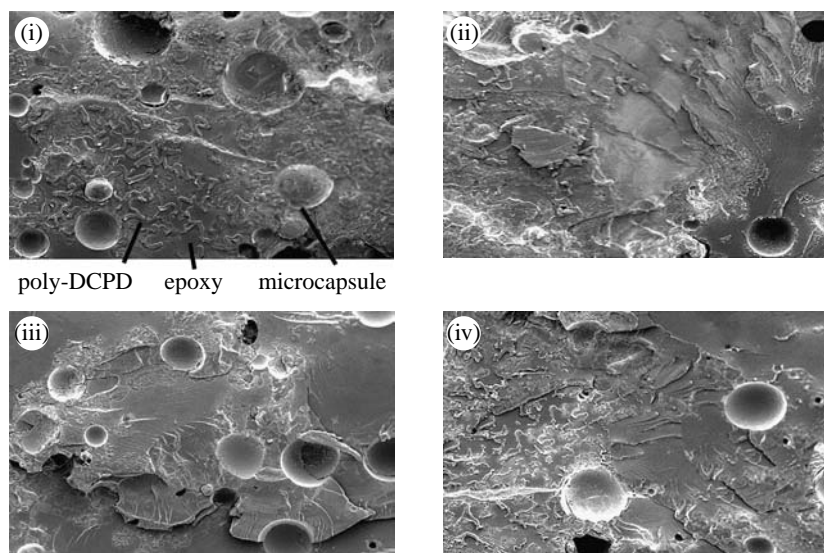


Figure 7. SEM of the fracture plane of a self-healing polymer correlating to curve E of figure 6. In all images, the crack is travelling from left to right. The width of each image represents 1 mm. (i) Fracture surface covered densely with poly-DCPD, (ii) fracture surface with occasional regions lacking poly-DCPD, (iii) fracture surface with adhesively bonded epoxy from the opposite fracture plane resulting in the retardation of crack growth rate and (iv) fracture surface showing occasional regions of poly-DCPD and significant uncovered areas.

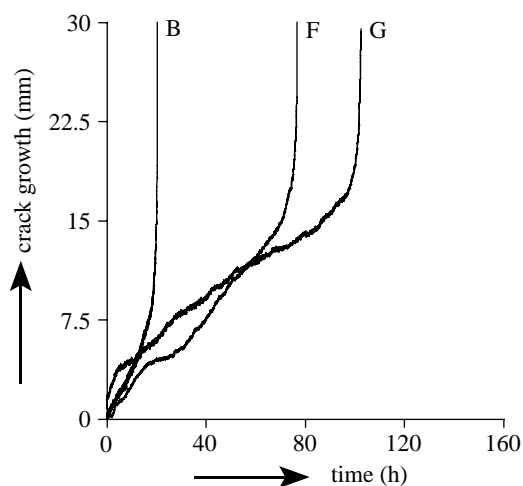


Figure 8. Fatigue at $K_{\max}=0.676 \text{ MPa m}^{1/2}$, $R=0.1$, $f=5 \text{ Hz}$ of TDCB polymer specimens. B, contains 20 pph microcapsules; F, contains 20 pph microcapsules and 5 pph of wax microspheres; G, contains 20 pph microcapsules and 2.5 pph of recrystallized catalyst (non-solvent addition).

considered previously by Brown *et al.* (2002) in which no healing took place at the largest loads ($K_{\max}/K_{IC}=0.5$) unless a rest period was provided. Above this value, only unstable crack growth occurred followed by rapid failure.

The faster chemical kinetics exploited in the current experiments enable significant lifetime extension at these higher load levels where the mechanical kinetics of crack growth dominate. For lower K_{\max} values, the crack growth rate is reduced and the chemical kinetics dominate and extend the fatigue life dramatically. Figure 9 shows data for the wax encapsulated catalyst specimens at a K_{\max} of $0.50 \text{ MPa m}^{1/2}$ ($K_{\max}/K_{IC}=0.45$). At this load level, complete arrest of the crack is achieved with the faster healing system, whereas the previous healing system

Table 1. Life extension factor of self-healing polymers with $K_{\max}=0.676 \text{ MPa m}^{1/2}$, $R=0.1$, $f=5 \text{ Hz}$. λ^* , life extension with respect to neat polymer and λ^{**} , life extension with respect to polymer with microcapsules.

specimen	type	life (h)	λ^*	λ^{**}
A	neat	4.8	0	n.a.
B	microcapsule only	20.2	3.3	0
C	wax with as-received Grubbs' catalyst	84.8	16.8	3.2
D	wax with recrystallized Grubbs' catalyst	124.2	25.1	5.1
E	wax with freeze-dried Grubbs' catalyst	156.4	31.9	6.7
F	wax microspheres without Grubbs' catalyst	76.6	15.1	2.8
G	recrystallized Grubbs' catalyst without wax	102.6	20.6	4.1

with slower polymerization kinetics would have provided a life extension factor $\lambda < 3$.

At lower loading levels where the chemical kinetics dominate, even under continuous fatigue the polymeric system autonomically responds by increasing its endurance limit and permanently arresting crack growth. At intermediate loading levels, self-healing systems that are chemically tuned to have faster healing kinetics provide greater life extension (see figure 6). As the healing kinetics are further accelerated, even greater fatigue extension can be expected. In general, if the healing kinetics are sufficiently rapid, fatigue cracks are effectively arrested as the material is exercised. This improved resistance to fatigue crack growth with accelerated healing kinetics is summarized in figure 10.

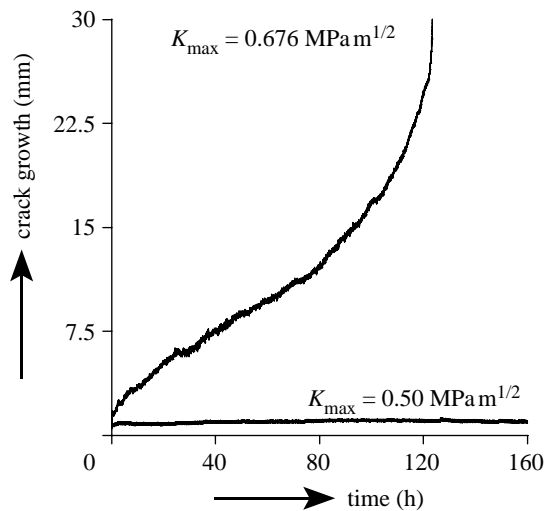


Figure 9. Fatigue crack growth at $K_{\max}=0.50 \text{ MPa m}^{1/2}$ ($K_{\max}/K_{\text{IC}}=0.45$) is completely arrested with accelerated healing kinetics. Fatigue crack growth at $K_{\max}=0.676 \text{ MPa m}^{1/2}$ is included for reference.

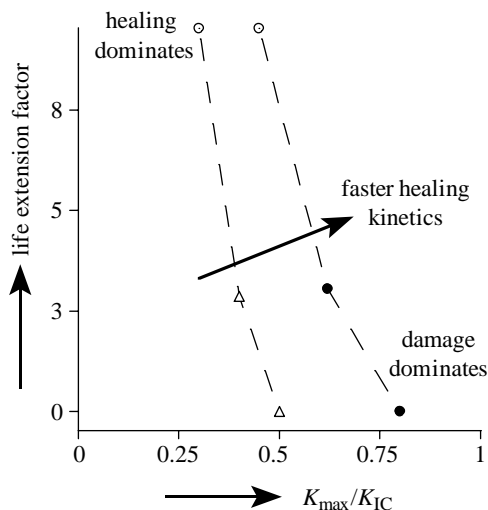


Figure 10. Faster healing kinetics result in improved fatigue crack growth resistance. Loadings that previously caused fast crack growth ($K_{\max}/K_{\text{IC}}=0.45$) can be arrested, while under severe loading conditions the crack growth is significantly retarded. Filled circles, original data; open triangles, data from Brown *et al.* (2005); open circles with dot, complete arrest of fatigue crack achieved.

If the mechanical kinetics of fatigue crack growth are extremely rapid, the healing system does not have sufficient time to inhibit the crack propagation. Endurance training, by periodic exposure to stress, can lead to significant life extension and is governed by the interplay between the mechanical kinetics of crack propagation and the chemical kinetics of healing in the polymer. At such high loading levels, the mechanical kinetics dominate, and sufficient periods of rest must be incorporated into the training cycle for the materials system to adapt. The rest periods reduce the apparent fatigue crack propagation rate and allow time for the polymerization of the dicyclopentadiene. Figure 11 demonstrates the fatigue life extension of the polymeric system at high loading levels ($K_{\max}=0.801$). Two

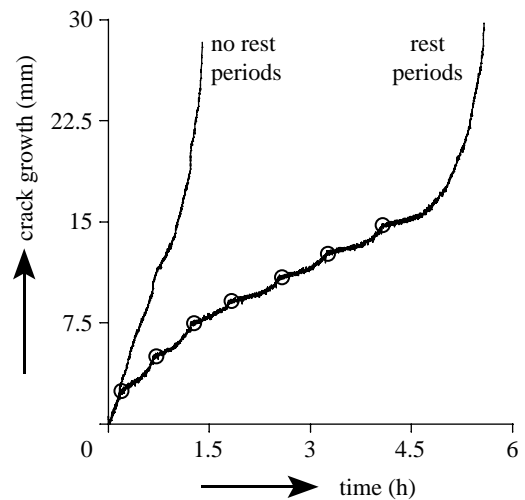


Figure 11. Fatigue with fast mechanical kinetics. $K_{\max}=0.801$, $R=0.1$, $f=5 \text{ Hz}$. Without rest periods, the specimen fractures quickly, with rest periods (indicated by circles) significant life extension is achieved.

identical specimens were loaded in fatigue, with one under continuous fatigue conditions and the other incorporating seven rest periods. The rest periods, which lasted for 10–12 h each, resulted in a fatigue life extension (λ) of 3, but the life extension of the fatiguing polymer will increase in proportion to the frequency of the rest periods.

4. CONCLUSION

Self-healing systems based on encapsulated healing agents and solid-phase catalysts can significantly extend the fatigue life of polymeric materials. Retardation of fatigue crack growth is achieved by a combination of crack-tip shielding mechanisms and increased toughness of the polymer system. At lower loading levels, the chemical kinetics of healing dominate and the materials system autonomously repairs the damage and arrests further fatigue crack growth. At intermediate loading levels, self-healing systems that are chemically tuned to have faster healing kinetics provide greater life extension.

A combination of protecting the catalyst with wax microspheres and using quickly dissolving catalyst morphologies leads to accelerated healing kinetics and results in greater life extension. Self-healing materials systems under extreme mechanical loading experiencing rapid fatigue crack growth can have significant life extension by incorporating rest periods into the loading history. Periodic application of rest periods during loading trains the material, effectively increasing its endurance limit. With this self-healing polymer technology, the incremental deterioration of polymeric materials can be stopped, or in the case of severe fatigue loading conditions, significantly slowed allowing for up to 30 times the life of a similar, but non-healing polymer.

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