

# EVALUATION OF A MODIFIED MATRIX AND THE SYNTHESIS OF THERMALLY REVERSIBLE SELF-HEALING MATRIX POLYMERS

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## Abstract

A modified epoxy matrix (with dissolved linear polymer) has been evaluated for thermal healing performance. The dissolved polymer healing agent is thought to dissolve through a matrix to a fracture surface at 140 °C, this has been visualized with scanning electron microscopy (SEM). Furthermore the healing ability of the samples cast from the modified matrix resin have shown to significantly reduce in performance on multiple healing cycles, in particular with high molecular weight healing agents. This is suggested to be due to the reduction in free volume within the matrix after thermal aging. In order to address this a new healing agent is required and the first precursor to a variety of thermally repairable cross-linked network polymers has been synthesized

## 1 Introduction

Highly cross-linked polymers in service as load-bearing materials are susceptible to mechanical and thermal degradation. Aerospace parts are expected to have a service life of over 25 years; during this time they might experience tens of thousands of flight hours and thousands of takeoff-landing cycles, all of which create stresses on the structural materials. In service, stresses or even impacts (dropped tools, bird collisions etc.) can cause damage to a composite material that is not easy to detect. Damage types include microcracks, fibre debonding and delaminations within the structure. Most of the time this damage is not critical and will not lead to immediate failure, but it may weaken the component and cause critical failure in the future. A material with intrinsic healing abilities allows the component to be repaired *in situ*; leading to a

substantial lifetime increase.

## 1.1 Modified Matrix Approach

Previous work at the University of Sheffield addressed this by adopting a modified matrix approach [1-2]. Upon heating we reported that a dissolved linear polymer is capable of diffusing through the matrix to bridge microcracks. This is a particularly elegant solution because it allows the use of industrial resin formulations and manufacturing techniques with the simple addition of a healing agent. The epoxy resin used (fig 1) was a diglycidyl ether of bisphenol-a (DGEBPA) and the corresponding healing agent (fig 2) is a polymeric analogue, poly(bisphenol a – co – epichlorohydrin).

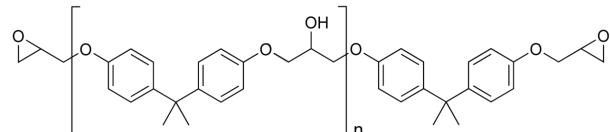


Fig 1. The structure of the epoxy resin used (Mw. 340 g mol<sup>-1</sup>).

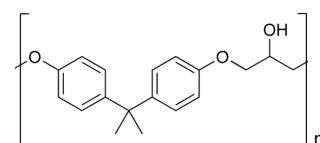


Fig 2. The structure of the healing agents used (Mw. 44,000 g mol<sup>-1</sup>).

The diffusion of the linear polymer can be tested by subjecting a fracture surface to scanning electron microscopy (SEM).

## 1.2 Thermally reversible polymers

Taking a new approach, the first steps are taken to build upon methodology established by Murphy et al [3] in 2008 in which a single component cross-

linked polymeric material has been produced from a dicyclopentadiene building block (fig 1). Upon heating the dicyclopentadiene core undergoes a thermally reversible retro Diels-Alder reaction to produce monomers with reactive cyclopentadiene end groups. During cooling the cyclopentadiene end groups react together to form a polymer. The polymer backbone is also capable of reacting with free cyclopentadiene groups to form cross-links. Localised heating upon or even within a polymer structure could be used to repair and theoretically perfectly reform damaged areas. As the healing mechanism is intrinsic to the polymer there is no parasitic weight. There are no inclusions, voids, or catalysts required; compared to, for example, a microencapsulation approach.

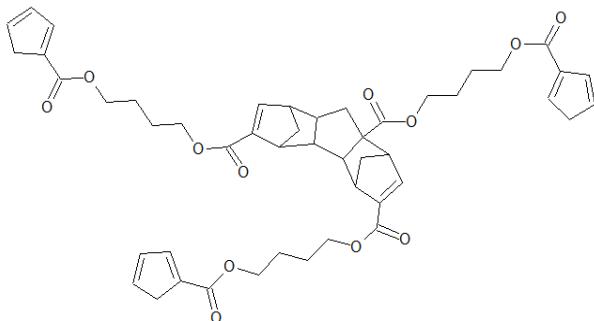


Fig 3. Example of a trimer formed via Diels-Alder cycloaddition.

### 1.3 Objectives

The primary aim of this work involves the investigation of the original modified epoxy resin matrix, the diffusion of the healing agent to a crack surface and the recovery in fracture toughness over multiple healing cycles.

The secondary aim of this ongoing work concerns the synthesis and evaluation of new potential healing agents based upon monomers that use the cyclopentadienyl functionality but vary considerably in their backbone. The materials produced have potential applications, after optimization and upscaling of the synthetic route, as reworkable engineering polymers. In the future the hope is to produce variants of these monomers that are compatible with industrial epoxy formulations. Such a healing agent dissolved within a locally heated thermoset matrix [4] can break down into mobile monomeric units which are able to easily diffuse

across microcracks without suffering from chain entanglements as with the present system. After cooling, the repair is facilitated by the reformation of the polymer network.

The synthesis (fig 4) is a modified version of the approach documented by Murphy et al [3] involving the air-free reduction of dicyclopentadiene to a reactive sodium cyclopentadienyl anion using elemental sodium followed by carboxylation with dry ice to form dicyclopentadiene dicarboxylic acid. The carboxylic acid groups are converted to the corresponding acid chlorides using thionyl chloride and the final step is a bislactonization reaction involving a variable diol.

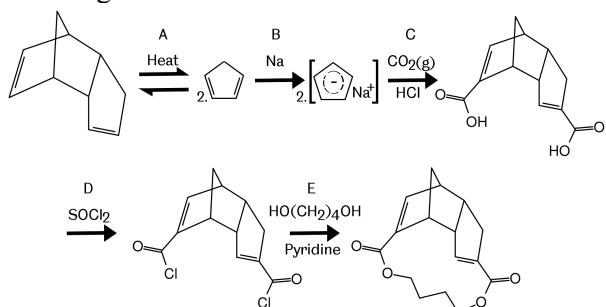
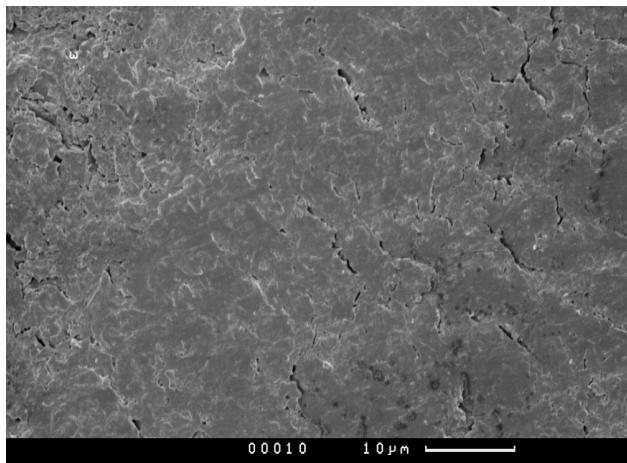


Fig 4. The synthesis of the monomer unit, precursor to the thermally repairable polymer.

## 2 Results and Discussion

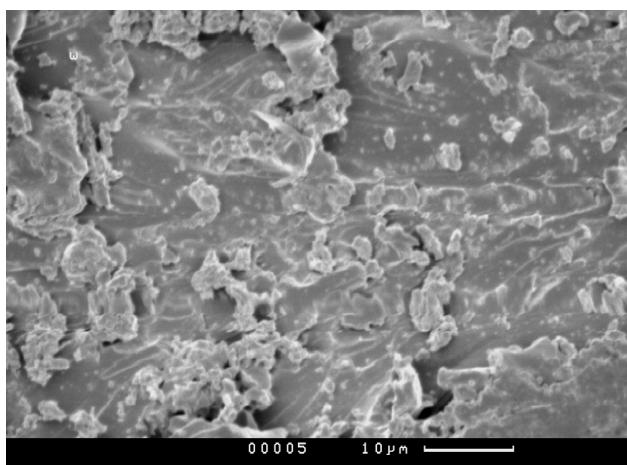
### 2.1 Modified Matrix

The modified matrix approach [1-2] assumes the mechanism for self-healing to be due to the diffusion (reptation) of a polymer to a crack surface in order to form chain entanglements and so close the crack. This assumption is supported by SEM on a fracture surface before and after healing cycles. The control samples (not pictured) show no significant change in the surface before and after a healing cycle. The modified (7.5 wt% healing agent) shows a much rougher surface after healing (fig 6) compared to before (fig 5). This is likely to be due to the healing agent that has diffused through to the surface.



**Fig 5.** SEM micrograph of a fracture surface, on a compact tension specimen, made from the modified resin (7.5% healing agent) **before any healing treatment**.

Scale bars 10  $\mu\text{m}$ .



**Fig 6.** SEM micrograph of a fracture surface, on a compact tension specimen, made from the modified resin (7.5% healing agent) **after 3 healing cycles**. Scale bars 10  $\mu\text{m}$ .

Tables 1 and 2 show the recovery of the modified matrix samples in fracture toughness, measured with compact tension testing where the  $K_{IC}$  is the critical stress intensity factor. Two different molecular weight healing agents are presented compared to a control with no healing agent. Table 1 shows the recovery in fracture toughness with a healing cycle length of 4 hours. Table 2 shows the recovery in fracture toughness with a healing cycle length of 10 hours.

Number of 4 hour healing cycles	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) No healing agent.	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) Sample with $6100 \text{ g mol}^{-1}$ healing agent.	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) Sample with $44,000 \text{ g mol}^{-1}$ healing agent.
0	$0.77 \pm 0.03$	$0.71 \pm 0.06$	$0.74 \pm 0.05$
1	$0.08 \pm 0.02$	$0.41 \pm 0.06$	$0.36 \pm 0.06$
2	$0.04 \pm 0.01$	$0.31 \pm 0.04$	$0.26 \pm 0.03$
3	$0.04 \pm 0.00$	$0.23 \pm 0.02$	$0.19 \pm 0.02$

Table 1 . Compact tension results (4 hour healing cycles each at 140 °C).

Number of 10 hour healing cycles.	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) No healing agent.	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) Sample with $6100 \text{ g mol}^{-1}$ healing agent.	$K_{IC}$ (MPa $\text{m}^{1/2}$ ) Sample with $44,000 \text{ g mol}^{-1}$ healing agent.
0	$0.77 \pm 0.03$	$0.71 \pm 0.06$	$0.74 \pm 0.05$
1	$0.11 \pm 0.02$	$0.43 \pm 0.06$	$0.46 \pm 0.06$
2	$0.03 \pm 0.00$	$0.26 \pm 0.03$	$0.26 \pm 0.03$
3	$0.04 \pm 0.01$	$0.18 \pm 0.02$	$0.12 \pm 0.02$

Table 2 . Compact tension results (10 hour healing cycles each at 140 °C).

The data shows that for the lower molecular weight ( $6100 \text{ g mol}^{-1}$ ) healing agent a shorter time (4 hours) is sufficient to obtain maximum recovery. The higher molecular weight healing agent gives a larger recovery but requires a longer healing cycle. The small amount of healing present in the control sample can be attributed to some slight post-cure. Consequently this has highlighted a limitation in this approach. The linear polymer is required to have a high molecular weight in order to give sufficient recovery in mechanical properties after healing. Such a high molecular weight polymer also suffers a kinetic penalty causing requiring a longer heat treatment due to the reduction in its mobility. Another trend that is shown by the data is that after repeated healing the recovery in fracture toughness is reduced each time. This is even more dramatic in the data from the 10 hour healing cycles. This effect could be explained by the physical aging of

the epoxy matrix.

Physical aging of an epoxy matrix is a process in which the polymer chains rearrange to approach the lowest energy equilibrium conformation [5]. At low temperature a large kinetic barrier exists; however, through this process repeated heating cooling cycles can cause a reduction in unoccupied volume within the matrix.

In the modified matrix approach a reduction in unoccupied volume reduces the mobility of the healing agent which could be the cause of the reduction of healing efficiency in the repeated healing cycles [6]. It would be beneficial, therefore, to produce a healing agent with increased mobility at the healing temperatures without sacrificing the mechanical properties. One possible way to overcome these limitations would be to use, as a healing agent, a polymer that is capable of dissociating into smaller mobile units at the healing temperature but at lower temperature is part of a three dimensional polymer network.

## 2.2 The Synthesis

Work in the area so far has concerned the optimization of the first step (the production of the DCPD dicarboxylic acid). The acid has been produced in moderate yield (20%) on a standard nitrogen double manifold. Work on optimizing this synthetic procedure and synthesis of the polymers is ongoing.

## 3 Conclusion

The modified matrix as an approach for the repair of polymers has been shown to be ineffective after multiple healing cycles. This is thought to be due to the reduction in free volume within the matrix as a result of physical aging.

In the search for a healing agent that would be able to overcome this problem the first precursor to a variety of thermally repairable cross-linked network polymers has been synthesized.

## 4 Experimental

### 4.1 Modified matrix

To produce the modified matrix, the healing agent poly(bisphenol-A-co-epichlorohydrin) was mixed

and into the epoxy resin (Epikote 828, Delta resins) under the mechanical stirrer at 90 °C for approximately 24 hours or until the mixture appears homogeneous with no evidence of undissolved thermoplastic. The mixture is then degassed under vacuum. The cure was facilitated by adding nadic methyl anhydride (NMA) (Robnor Resin, UK) hardener, 44% into the mixture and stirred for 15 minutes followed by Benzylidimethylamine (BDMA) (Robnor Resin, UK) (1.1%) for 5 minutes. The testing of the ability of the modified matrix to heal was carried out using compact tension testing, with samples being prepared according to BS13586:2000 [7]. The healing cycle involves lightly clamping the two sides of the sample in place and heating at 140 °C for 4 or 10 hours before cooling to room temperature at a rate of 2 °C min<sup>-1</sup>.

Scanning Electron Microscopy (SEM) was performed using a Camscan Mk 2 model SEM. The SEM photo-micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 5 kV, resolution of 4 nm. For sample preparation, the pieces of cured resin; with dimension of 5 × 2 × 2 mm<sup>3</sup>, were cut from the fracture surface of compact tension specimen and covered with conductive paint.

### 4.2 Synthesis of a dicyclopentadiene dicarboxylic acid.

A reactive distillation of the dimer dicyclopentadiene (50 ml, Sigma-Aldrich) (DCPD) to cyclopentadiene (CPD) is established at ~150 °C using a lagged vigreux column. Meanwhile, sodium (8g, Sigma-Aldrich) is cut into small (~5 mm) pieces under diethyl ether and added to a three-necked round bottom flask which is kept under nitrogen. The excess ether is removed via a syringe and dry tetrahydrofuran (~100 ml) (THF) is added. When most of the DCPD has distilled cool both flasks to 0 °C and then transfer the CPD (~36.46 g) via canula into the stirred mixture of sodium and THF. Allow the mixture to slowly heat up to ambient temperature over night. It is vital to ensure that the system is oxygen free at this point otherwise the yield is greatly reduced and the solution turns brown instead of deep red.

Increase the stirring to vigorous and then bubble CO<sub>2</sub> gas (formed from the sublimation of dry ice) through a gas washer bottle containing concentrated

sulphuric acid and into the reaction vessel. Immediately the viscosity will increase as the reaction takes place necessitating the eventual use of an overhead stirrer through a teflon seal. Leave the reaction for at least 4 hours to ensure all the sodium cyclopentadiene has reacted. Remove the residual THF from the vessel via a vacuum and dissolve the resulting solid in distilled water (~ 300 ml). The solution is extracted (3 x 100 ml) chloroform and filtered to remove any insoluble impurities. Acidify the aqueous layer with 10% hydrochloric acid and collect the precipitate. The precipitate is recrystallised from methanol to produce an off white solid 12.51g (20% based on the CPD) (M.p. 205-208 °C). <sup>1</sup>H NMR (d-DMDO, 400 MHz): δ 1.37 (d, 1H), 1.52 (d, 1H), 1.89 (d, 1H), 2.30 (m, 1H), 3.11 (s, 1H), 3.18 (s, 1H), 3.48 (m, 1H), 6.40 (d, 1H), 6.72 (d, 1H), 12.18 ppm (s, 2H). <sup>13</sup>C (d-DMSO, 400 MHz): 33.13, 40.68, 46.54, 47.28, 50.57, 54.26, 138.61, 139.51, 142.91, 147.26, 166.12, 166.38 ppm.

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