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Performance of self-healing epoxy with microencapsulated healing agent and shape memory alloy wires

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ABSTRACT

We report the first measurements of a self-healing polymer that combines a microencapsulated liquid healing agent and shape memory alloy (SMA) wires. When a propagating crack ruptures the embedded microcapsules, the liquid healing agent is automatically released into the crack where it contacts a solid catalyst embedded in the matrix. The SMA wires are then activated to close the crack during the healing period. We show that dramatically improved healing performance is obtained by the activation of embedded SMA wires. We conclude that improved healing is due to a reduction of crack volume as a result of pulling the crack faces closed, and more complete polymerization of the healing agent due to the heat produced by the activated SMA wires.

1. Introduction

Damage to engineering materials in service eventually causes them to wear out or fail. Until recently, the only solution was manual repair or replacement of the damaged component. However, new materials that self-heal are now being developed. Self-healing composites could be especially important for the aerospace sector, for example, in cases where internal damage is difficult to detect, or where it is impossible to carry out field repairs. Automatic repair during service would also provide more reliable and safer aerospace structures.

The first self-healing polymer was reported by White et al. [1], based on a liquid healing agent (dicyclopentadiene, DCPD) contained in urea–formaldehyde (UF) microcapsules [2] and a solid catalyst (Grubbs' first generation catalyst), both dispersed in an epoxy matrix. In this material, a propagating crack ruptures the microcapsules in its path, releasing the low-viscosity healing agent, which then covers the crack plane by capillary action and polymerizes on contact with the catalyst via ring-opening metathesis polymerization (ROMP). Since the first demonstration, the microencapsulation system has been developed further and optimized. For example, smaller capsule sizes [3,4], improved catalysts [5,6] and alternative healing systems [7,8] have been investigated. In a separate approach to the delivery system, Trask et al. embed hollow glass fibers in a composite material, infused with either resin or curing agent (Cycom 823 two-part system) [9,10]. The fibers rupture on impact, releasing the components into the damaged region. Toohey et al. have shown that delivery of healing agents via a microvascular network will enable multiple healing events [11].

The materials system reported in this paper is based on the White et al. microcapsule approach [1]. Following established protocols [12,13], the performance is evaluated by measuring the peak load required to re-fracture a tapered double cantilever beam (TDCB) sample, after healing. In previous studies [3,13] we have shown that the healing performance depends on the fill factor (γ) [13], defined as:

$$\gamma = \frac{V_h}{V_c} \tag{1}$$

where V_h and V_c are the volume of the delivered healing agent and of the closed crack, respectively. For optimum healing, $\gamma > 1$ and the healed peak load is maximum. For epoxy healed at room temperature, the healing efficiency peaks at about 50% with respect to the virgin material [3]. However, the healed peak load drops off rapidly when $\gamma < 1$. A technique is therefore needed to minimize the crack volume and ensure optimal healing even with small amounts of delivered healing agent.

Shape memory alloy (SMA) wires can provide this function in a self-healing material. In a previous study [13] SMA wires bridging a crack were activated during healing, exerting a closure force of several Newtons per wire. Samples containing SMA wires that were manually injected with DCPD healing agent showed an increase in average healed peak fracture load from about 38 N to 60 N,

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corresponding to an increase of healing efficiency from 49% to 77%. The improvement in healing efficiency is due to the reduced crack volume and to heating of the SMA wires during activation. In this paper we report that comparable improvements in healing performance are observed with SMA wires when the healing agent is delivered autonomically from microcapsules.

2. Experimental methods

2.1. Microcapsule thermal stability

Microcapsules containing DCPD healing agent were fabricated as described in Ref. [2]. Their thermal stability was assessed by thermogravimetric analysis (TGA). Samples of microcapsules (10–20 mg) were weighed in a 150 μl ceramic crucible and then placed in the TGA. The TGA was heated from 25 °C to 600 °C at a rate of 10 °C/min, under a controlled nitrogen environment, while continuously monitoring the sample mass.

2.2. Fracture behavior of polyDCPD healing agent

The fracture behavior of polyDCPD was evaluated by compact tension (CT) testing following ASTM standard D 5045–91a (Fig. 1). To prepare the samples, DCPD was mixed with 5 wt% Grubbs' catalyst wax microspheres (containing 10 wt% catalyst and 90 wt% wax) and cast in an aluminum mold to form a polymer plate. Two types of samples were prepared to simulate the different types of healing cycles. The first plate was allowed to polymerize at room temperature for 24 h. The second plate was placed in an oven at 80 °C for the first 30 min after mixing to simulate the effects of the heating cycle of the SMA wires (§2.3), and then left at room temperature for 24 h.

Four CT samples were machined from each plate. Each sample notch was sharpened by scoring with a razor blade, forming a pre-crack. The pre-crack length was measured for each sample, and was typically 0.1–0.3 mm. The samples were then individually mounted in a tensile tester and loaded in tension at a constant displacement rate of 5 μm/s, until failure, recording the force, P (N) as a function

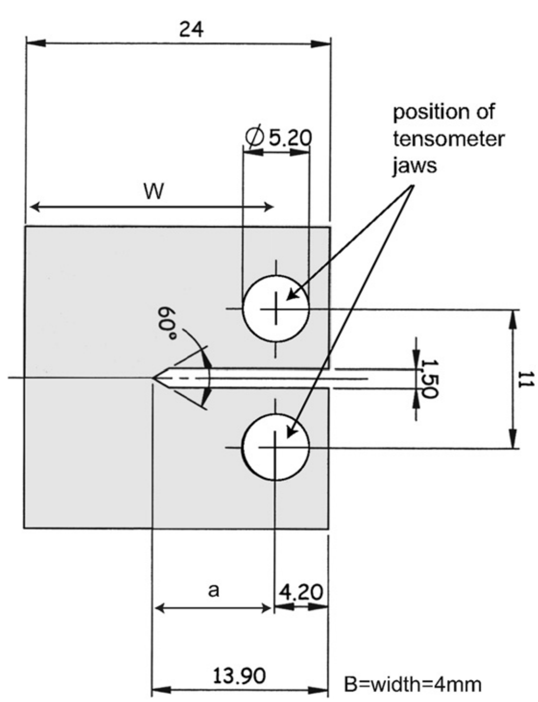

Fig. 1. Compact tension (CT) sample geometry (distance units are mm).

of time. The characteristics of the force–displacement plots of the two sample types were then compared. The fracture characteristics of the two sample types were also compared with scanning electron microscope (SEM) images of the fracture planes.

For the samples that followed linear elastic fracture mechanics, the fracture toughness, K_{IC} (MPa m$^{1/2}$), was calculated from the expression:

$$K_{IC} = \frac{P_C}{BW^{1/2}} f(x) \tag{2}$$

where, P_C (N) is the critical load for crack propagation, B (m) is the sample width, W (m) is the distance between the centre of the loading slot and the back end of the sample, and

$$f(x) = \frac{(2+x)\left(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4\right)}{(1-x)^{3/2}} \tag{3}$$

where $x = a/W$, $0.2 < x < 0.8$ and a includes the length of the pre-crack.

2.3. Healing performance of SMA/microcapsule self-healing epoxy

For all self-healing tests the matrix material was EPON 828 resin (Shell Chemicals) cured with diethylenetriamine (DETA; Sigma–Aldrich) in a 100:12 mass ratio. The properties of the SMA wires (Furukawa Electric) are summarized in Table 1. The transformation temperatures were determined by differential scanning calorimetry.

The self-healing properties were investigated using samples with a tapered double cantilever beam (TDCB) geometry (Fig. 2), first developed by Mostovoy et al. [14]. This technique provides a measurement of the fracture toughness that is independent of the initial crack length, i.e.

$$K_{IC} = \alpha P_C \tag{4}$$

where $\alpha = 11.2 \times 10^3\ \mathrm{m}^{-3/2}$ for the present geometry [12]. Three SMA wires were each tensioned with a 50 g mass and embedded at the mid-plane of the sample, perpendicular to the crack direction (Fig. 2). Microcapsules of typically 100–200 μm diameter were prepared, containing DCPD healing agent [2]. The microcapsules were added into the epoxy matrix in a 5, 10 or 20 wt% concentration. Grubbs' first generation catalyst (Sigma–Aldrich) was recrystallized via a non-solvent addition method [15] and wax-encapsulated for protection [5], to form 10 wt% Grubbs' catalyst in wax microspheres of 200 μm average size. The microspheres were added into the epoxy matrix in a 5 wt% concentration. In order to minimize costs, the microspheres were localized around the crack plane region (Fig. 2) [3]. The resin was degassed, cured in silicone rubber molds for 24 h at room temperature, and post-cured at 35 °C for a further 24 h. After post-curing, a sharp pre-crack was made by tapping a razor blade into the molded starter-notch.

Table 1
Properties of the SMA wires used in the present study. M_s and M_f are the start and finish temperatures, respectively, of the martensite-to-austenite (forward) transformation. A_s and A_f are the corresponding temperatures of the austenite-to-martensite (reverse) transformation.

Composition (Ni:Ti:Cu)	44.86:45.08:10.06
Diameter	150 μm
M_s	53.6 °C
M_f	47.1 °C
A_s	59.8 °C
A_f	65.6 °C