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Improving solvent-based self-healing materials through shape memory alloys

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ABSTRACT

Healing of epoxy resins can be accomplished using a combination of embedded ethyl phenylacetate (EPA) solvent loaded capsules and shape memory alloy (SMA) wires. Upon crack formation, the EPA solvent diffuses in the resin and induces swelling which tends to close the crack, while the SMA wires upon heating reduce the crack gap and foster residual epoxy cure. The kinetics of EPA diffusion in the epoxy matrix were measured so as to evaluate the swelling thickness versus time, and concentration at saturation. The largest healable crack gap was found to be 30 μm after 24 h. EPA solvent was shown to lower the curing reaction kinetics and the glass transition temperature (T_g) of the epoxy, as well as its stiffness and strength. Healing efficiency was assessed using long-groove tapered double cantilever beam (TDCB) test samples, with embedded SMA wires across the crack plane. The healing efficiency greatly improved when the crack gap was reduced to 30 μm, from 24% for samples without SMA wires to 78% for samples with SMA wires activated according to an optimized scenario.

1. Introduction

Self-healing materials exhibit the ability to repair themselves and to recover functionality using the resources inherently available to them [1–3]. Two primary classes of self-healing have emerged: intrinsic and extrinsic systems [4]. Intrinsic systems recover from damage through an inherent property of the material (e.g. increasing molecular mobility by heating a thermoplastic above its glass transition temperature (T_g) or exploiting reversible crosslinking reactions). Extrinsic systems rely on incorporating secondary materials (healing agents), usually a liquid phase, that is released upon damage and fills the damage volume. A similar classification scheme was introduced by Bergman et al., who distinguished between reversible and irreversible systems [5]. In almost all cases, intrinsic systems can repeatedly heal damage, so that healing can occur more than once at the same location because the mechanism is based on a reversible chemical or physical process. On the other hand, extrinsic systems are irreversible as the healing agent is depleted after a healing event. An exception to this rule is microvascular delivery systems, where the healing agent is continuously provided through a network of microchannels [6–13]. While intrinsic systems only heal when the crack faces are in close contact as the molecules cannot bridge large crack gaps, extrinsic systems demonstrated healing for larger crack gaps, depending on the accessible volume of healing agent within the damage zone [14]. Furthermore, intrinsic systems mostly rely on heating to induce healing. Depending on the chemical systems, these temperatures are often in excess of 100 °C. As an example, reactions of the Diels–Alder (DA) type have a threshold temperature at which the two components dissociate at about 150 °C [2]. When cooling down, the bonds are reformed through the reverse Diels–Alder (rDA) reaction. The heat–cool cycle also leads to a loss of mechanical properties of the affected area during heating.

The extent of the damage to repair is critical in selecting an appropriate repair strategy. Small damage in coatings or microcracks could be healed with intrinsic systems while macroscopic damage with substantial crack volume needs an extrinsic system. Whichever approach is used, reducing the damage volume is beneficial to improving healing performance and reducing the required volume of healing agent. Kirkby et al. [15] investigated the effect of reducing crack separation by activating embedded shape memory alloy (SMA) wires to close the crack in epoxy fracture samples using a DCPD/Grubbs' healing system. Healing efficiency as measured through the recovery of fracture toughness was increased by a factor of 1.6 for manually injected samples through a combination of reduced crack gap and localized heating of the crack plane as a result of SMA wire activation. Fully in-situ healing was then demonstrated for self-healing epoxy with embedded DCPD microcapsules and Grubbs' catalyst particles [14]. The healing efficiency showed a strong dependency on the crack gap. For the smallest

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gaps, healed peak loads of 60 N were measured, representing 80% of the virgin properties. In stark contrast, for samples without SMA wires, the average healed peak load was only about 18 N.

Among the various healing systems investigated so far, some of these healing systems used diffusion based healing mechanisms. Hayes et al. [16] mixed up to 20% of a thermoplastic to an epoxy matrix which acted as a healing agent when heated. Mookhoek et al. [17] analyzed healing in a thermoplastic material, containing microencapsulated solvent as a healing agent. Caruso et al. [18] recently proposed a solvent-based healing system for thermosetting polymers (e.g. epoxy). Upon damage, the solvent is released onto the fracture surface, increasing local chain mobility and promoting the reaction of residual hardener with either residual epoxide groups in the matrix, or a small volume of epoxy resin delivered with the solvent [19]. While it was first demonstrated for chlorobenzene, a less toxic solvent (ethyl phenylacetate, or EPA) mixed with a few percent of epoxy was shown to yield nearly 100% healing efficiency and long term stability was preserved even after 30 days. However, this excellent healing efficiency was only achieved in a modified TDCB sample geometry that maintained crack faces in close contact after fracture, thus minimizing the damage volume to heal, known as short-groove TDCBs.

In this article, we evaluated the healing of epoxy using solvent microcapsules combined with embedded SMA wires. The combination of the two concepts should allow the healing of larger damage volumes as is encountered in standard TDCB geometries. To optimize the healing process, we investigated the mechanisms of solvent healing by analyzing the diffusion kinetics of the solvent in the epoxy matrix. We experimentally determined swelling of the thermoset resin due to the solvent diffusion and quantified the effect of the solvent on the matrix in terms of residual heat of reaction as well as mechanical properties. We finally investigated the effect of SMA wire activation on the healing efficiency of TDCB samples, for various configurations.

2. Materials and methods

2.1. Materials

The epoxy resin used was Epon 828, a DGEBA epoxy resin (Shell Chemicals). It was mixed with diethylenetriamine (DETA, Sigma–Aldrich) as a curing agent in a 100:12 ratio. Curing took 24 h at ambient temperature followed by 24 h at 35 °C. Ethyl phenylacetate (EPA 99%, Sigma–Aldrich) was used as the healing agent. The SMA wire used in this study was a martensitic NiTiCu alloy with respective composition of 44.86/45.08/10.06 and a diameter of 150 μm (Furukawa Techno Material). The phase transition temperatures were determined using differential scanning calorimetry (DSC). Any previous deformation history was erased by performing a first heat–cool cycle between 10 and 100 °C and the phase transition temperatures were then determined during a second heat–cool cycle between 10 and 120 °C. They are summarized in Table 1.

2.2. Encapsulation and stability

The microcapsules were produced using the protocol developed by Blaiszik et al. [20]. In the present work, the core liquid was composed of 97.5% EPA and 2.5% Epon 828 as this ratio was shown to provide the best healing efficiency through formation of additional thermoset material in the crack plane [19]. The emulsion was stirred at a rate of 400 rpm and after the urea-formaldehyde (UF) reacted to form the shell wall the microcapsules were dried in ambient air for at least 24 h, then mechanically sieved, retaining the fraction between 125 and 355 μm. The mean diameter was measured using optical microscopy, taking an average of at least 100 measurements. For comparison purposes, a batch of DCPD containing microcapsules was prepared using the protocol defined by Brown et al. and a stirring rate of 550 rpm [21]. Stability of microcapsules was evaluated by thermal gravimetric analysis (TGA) on a Mettler Toledo sDTA851e. The capsules were kept at ambient conditions for several days before running the TGA measurements, so moisture intake was possible. Capsules were loaded in the TGA and were heated from 30 to 400 °C at 10 °C/min in a N_2 atmosphere. The results were then related to the capsule stability by comparing the boiling temperatures of the core material to the capsule weight loss profile.

Table 1
Phase transition temperatures for the SMA wire.

	A_s	A_f	M_s	M_f
T [°C]	54.3	60.6	44.3	37.3

2.3. Solvent diffusion

The first set of experiments to quantify the swelling of epoxy in pure EPA solvent were carried out using cylindrical epoxy samples of 9.7 mm diameter and a height of 4.9 mm (ca. 0.42 g), which were immersed into the solvent. Weight uptake was measured using a high-resolution precision balance (Mettler Toledo AT261 DeltaRange, 0.01 mg reading, repeatability 0.015 mg). To do so, the samples were taken out of the solvent and dried on the surface using Kimtech Precision Wipes (Kimberly Clark, ref. 7552) before weighing. The error due to residual solvent on the sample surface was estimated to be less than 0.04% for this test configuration.

After 3 weeks of immersion in the solvent, the samples were cleaved along the axis of the cylinder and the crack faces were observed under a Olympus stereo-microscope. Presence of solvent in the diffusion layer was measured with an FTIR microscope (PerkinElmer Spotlight FTIR Imaging).

Since the diffusion kinetics of EPA in epoxy are relatively slow, a second set of experiments using smaller samples (from ca. 0.2 to 6 mg) were prepared in order to determine the solvent solubility at saturation. After 3 weeks immersion, these samples were dried on the surface, weighed, and weight uptake was calculated.

2.4. TDCB sample preparation

The long-groove TDCB sample preparation with integrated SMA wires followed the procedure described by Kirkby et al. [15] with minor modifications. The long-groove TDCB geometry is shown in Fig. 1. The samples were prepared in two steps: first the surrounding matrix including the SMA wires were cast into silicone molds using pure epoxy resin. After 4 h, the inner part of the sample was cast using epoxy resin mixed with 15 wt% of microcapsules containing the healing agent (97.5% EPA and 2.5% Epon 828). In parallel, to provide a benchmark for healing results, short-grove samples without SMA wires were also prepared. Short-groove samples are geometrically identical to the long-groove TDCBs, however the central groove only extends 25 mm from the notch allowing the crack to arrest after fracture so that the crack faces maintain registration and the crack gap is minimized [19].

Previously, Kirkby et al. [15] included clamps on the SMA wires at the surface of the TDCB specimen in order to ensure good load transfer of recovery force from the wires to the specimen. In this