Effect of confinement level and local heating on healing efficiency of self-healing particulate composites

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ABSTRACT

Shape memory polymer based self-healing materials are a special class of materials that have been the subject of much research over the past decade and many impactful discoveries have been made thus far. In a previous study (Compos. Sci. Technol. 2010; 70: 1419–1427) it was shown that in order for efficient healing, confinement during healing is essential. It was also shown that use of a two-step close-then-heal (CTH) method during healing of damaged shape memory particulate composites provided molecular scale healing. The present study further investigates the influence of confinement levels and local heating on the healing efficiencies of a polystyrene based shape memory polymer with 6% by volume of thermoplastic particle additives (copolyester as solid healing agent). The healing process was conducted by locally heating fractured cylindrical specimens at three levels of lateral (radial) confinements and axial constraints, and varying heating times. It is found that, lateral confinement levels, axial constraints, and heating times all control the healing efficiency. Almost complete strength recovery is obtained with 100% lateral confinement, 12 MPa axial constraint stress, and 60 min of heating time.

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1. Introduction

Crack formation and propagation in mechanical components has plagued the engineering and manufacturing industry for decades. As mechanical components are used, cracks may begin to form and propagate with continued use, and ultimately cause the component to fail, sometimes catastrophically. The problem is that many times cracks form without notice and through continued use of the component (cyclic loading) finally cause the component to fail. Damage due to impact is particularly problematic for fiber reinforced polymer composites because after the material has been impacted it may show no apparent damage on impact point and yet significantly damaged within. Self-healing materials offer a method of combatting this problem [1].

While a number of self-healing approaches and strategies have been explored for thermosetting polymers, and the literature is exploding, generally, healing can be divided into two categories. One is extrinsic healing based on incorporation of external healing agent; the other is intrinsic healing by polymer itself. As indicated by Li [2], both extrinsic healing and intrinsic healing can be further divided into physical healing (molecule entanglements) and chemical healing (reestablishment of chemical bonds). The chemical healing can be further divided into subcategories based on the type of chemical bonds (covalent bonds, hydrogen bonds, etc.).

Intrinsic healing systems include polymers with thermally reversible covalent bond (TRCB) [3], ionomer [4], supramolecule chemistry (hydrogen bonds, metal-ligand coordinations, $\pi-\pi$ stacking interactions) [5], thermosetting epoxy with unreacted epoxide [6], and dynamic covalent bond exchange (DCBE) [7]. However, not all the intrinsic self-healing polymers are suitable for applications in load carrying structures. The reason is that in load bearing structures, the polymer matrix must have sufficient strength and stiffness, even using fibers as reinforcement. Therefore, extrinsic healing systems by incorporation of external healing agent in thermosetting structural polymers have been developed. The healing agent can be liquid [8–13] or solid [14,15]. While the solid healing agent such as thermoplastic particles can be directly dispersed in a polymer matrix [16,17], liquid healing agent needs to be stored and released on demand through various containers such as microcapsules [18,19], hollow fibers [20–22], and biomimetic microvascular network [23,24]. This is a well-established research area, and is still growing very fast.

Based on Wool and O'Connor [25], for healing to occur, five

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stages of crack healing are needed, including (a) surface rearrangement; (b) surface approach; (c) wetting; (d) diffusion; and (e) randomization. For a lot of healing systems, the fractured specimens are usually manually brought into contact before healing starts. As indicated by Wool [26], and echoed by Binder [27] and Li [2], this simple operation represents the largest challenge in the real world applications. Obviously, one cannot bring a fractured skin panel together by hand in a Boeing aircraft. One may not be able to bring a fractured specimen together manually if the boundary of the specimen is fixed. If the specimen is forced to bring in contact, new damage may occur. Therefore, one grand challenge for both extrinsic healing and intrinsic healing is how to bring the fractured surfaces in contact before healing starts.

In 2008, Li and John [28] used shape memory effect to repeatedly close impact induced cracks in a sandwich composite. This idea was also extended to close impact induced cracks in grid stiffened composite [29] and 3-D woven fabric reinforced composite [30]. Later Li and Nettles [31] and Li and Uppu [32] proposed the two-step healing scheme, close-then-heal (CTH), by mimicking the self-healing mechanism of human skin; see Fig. 1. In this scheme, the shape memory polymer matrix was compression programed before service. Once a crack is created within the shape memory polymer matrix, heating triggers constrained shape recovery of the matrix, which helps close the crack, and melting, wetting, diffusion, and randomization of the embedded thermoplastic heal the narrowed or closed crack molecularly. It is noted that, in addition to closing cracks by compression programmed SMP matrix, crack closing can also be achieved by dual-functional polymeric system [33]. For conventional thermosetting polymers without shape memory effect, crack closing can be achieved by embedding pre-stretched SMP fibers [34], shape memory alloy (SMA) wires [35], and fishing line based polymeric artificial muscles [36]. It has been proved that this CTH scheme can heal structural scale cracks repeatedly, molecules, timely, and with a small amount of healing agent (as low as 3% by volume) [16]. However, as indicated by Li and Uppu [32], a key requirement for CTH is that external constraint must be applied to effectively close the crack. And yet, it is not clear how the constraint level affects the healing efficiency. Also, in previous studies, the entire specimen or panel was heated to trigger constrained shape recovery, which is obviously impractical in real world structures. For example, one cannot heat the entire Boeing 787 in order to heal a crack at the tip of the wing.

The purpose of this study is to evaluate the effect of the level of external constraint and local heating time on the healing efficiency of a thermoset shape memory polymer based particulate composite, *per* the CTH scheme.

2. Experimentation

2.1. Raw materials

The material used in this study was a particulate composite. This material consisted of a polystyrene shape memory polymer (PSMP) matrix dispersed with copolyester thermoplastic particle additives (CP). Synthesis of the PSMP material was achieved by mixing vinylbenzene (Aldrich, Reagentplus ≥99%), vinyl neodecanoate (Aldrich), divinyl-benzene (Aldrich, technical grade, 80%, mixture of ionomers) and polystyrene-*block*-polybutadiene-block-polystyrene (Sigma-Aldrich, Styrene, 30 wt %). Benzoyl peroxide (Sigma-Aldrich, Luperox® A98, reagent grade, ≥98%) was used as the radical initiator. The thermoplastic particle additive was a linear copolyester (CP) consisting of Terephthalic acid, Isophthalic acid, and 1,4-Butanediol (Abifor Inc., Switzerland). The copolyester possessed the following properties: particle size ≤80 μm, density 1.3 g/cm^3, glass transition temperature T_g 16 °C, melting temperature T_m range 114–124 °C, and bonding temperature T_b range 125–150 °C. As a healing agent, the healing temperature needs to be in the range of T_b in order to have sufficient physical entanglement between the healing agent molecules and the PSMP molecules.

2.2. CP-PSMP composite fabrication and specimen preparation

The fabrication of the CP-PSMP composite was achieved through a strategic mixing process followed by curing of the final material in an oven. To begin the process, vinylbenzene and polystyrene were added to a three-necked flask equipped with a mechanical stirrer. The mixture was then stirred for 30 min using a polytetrafluoroethylene stirrer. The remainder of the process was: divinyl-benzene was added and stirred for 30 min, vinyl neodecanoate was added and stirred for 30 min, 6% by volume of thermoplastic particles were added and stirred for 1 h, and lastly benzoyl peroxide was added to the reactant to serve as the reaction initiator. The mixture was again stirred for 30 min. The mixture was then degassed in a Sargent-Welch vacuum (Welch brand, Duo-seal, Model NO. 1402 Ac-2065) at a 0.1–0.2 KPa vacuum for 30 min. After degassing, the mixture was poured into rectangular curing molds constructed from polytetrafluoroethylene. The top surface of the material was sealed using a polytetrafluoroethylene sheet. The material was cured as per the following scheme: 16 h at 75 °C, 10 h at 80 °C, and 5 h at 110 °C. After curing the composite was allowed to cool to room temperature after which it was demolded.

The cured rectangular slabs were cut into cylindrical specimens measuring 152 mm in length and having a 10 mm diameter. The shape and dimensions were chosen to comply with ISO178 standard for 3-point flexural tests. Also, the cylindrical shape removes any singularities within the specimen and provides uniform heat distribution during heating.

2.3. Differential scanning calorimetry (DSC) analysis

The T_g of the CP-PSMP composite was determined via differential scanning calorimetry analysis. A 6.20 mg sample of the CP-PSMP composite was placed in the sample pan in the Perkins Elmer DSC 4000 machine. The material was first held at 30 °C for 1 min before it was cooled to −70 °C at a rate of 20 °C/*min*. The sample was then held for 30 min at −70 °C after which it was heated to 230 °C at a rate of 10 °C/*min*. It was then held at 230 °C for 1 min before again being cooled to −70 °C at a rate of 20 °C/*min*. This heating and cooling cycle was performed two times and the
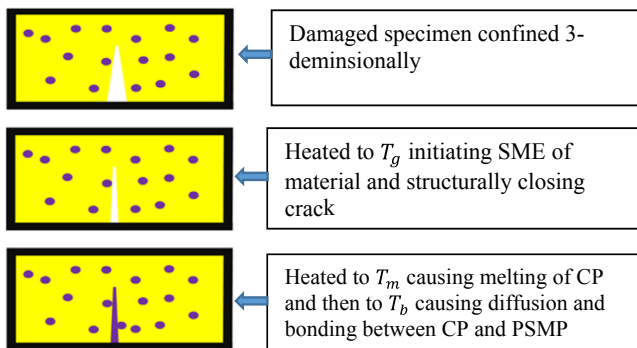

Fig. 1. Close-then-heal (CTH) scheme [2]. The golden color represents the polystyrene shape memory polymer (PSMP) and the purple dots represent the copolyester (CP) thermoplastic particles of the composite material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The three panels of Fig. 1 contain the following labels:
- Damaged specimen confined 3-deminsionally
- Heated to T_g initiating SME of material and structurally closing crack
- Heated to T_m causing melting of CP and then to T_b causing diffusion and bonding between CP and PSMP