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Effect of strain hardening of shape memory polymer fibers on healing efficiency of thermosetting polymer composites

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ABSTRACT

Recently, shape memory polymer fibers (SMPFs) have been used in a biomimetic two-step (Close-Then-Heal) self-healing system for healing macroscopic cracks. The objective of this study was to investigate the effect of cold-drawing programming of SMPFs on the healing efficiency of conventional thermosetting polymer composites and the possibility of healing wide-opened crack by localized heating. To achieve the objective, continuous SMPF strand reinforced conventional epoxy composite beam specimens, which were dispersed with thermoplastic particles, were prepared. The SMPF strands were cold-drawn to various pre-strain levels before casting the polymer matrix. Repeated fracture/healing test was conducted by uniaxial tension. It is found that the composites were able to repeatedly heal macroscopic cracks. Strain-hardening by cold-drawing increased the healing efficiency considerably. It was demonstrated that healing can be achieved by heating locally surrounding the cracked region. The mechanism for the enhanced recovery stress was due to cold-drawing induced molecular alignment and formation of some perfect crystals in the hard segment domain of the SMPF.

1. Introduction

Damage-healing of polymer composite materials has been a topic of intensive research for over a decade [1–5]. Basically, healing can be divided into two categories. One is based on incorporation of external healing agent; the other is intrinsic healing by polymer itself. For incorporation of external healing agent, the agent can be liquid [6,7] or solid [8,9]. While the solid agent such as thermoplastic particles can be directly dispersed in a polymer matrix [8–11], liquid healing agent can be stored and released on demand through various approaches such as microcapsules [12,13], hollow fibers [14,15], and biomimetic microvascular network [16,17]. For intrinsic healing systems, they include polymers with thermally reversible covalent bond [18], ionomer [19], hydrogen bond [20], etc. This is a fast growing area with ample supply of literature.

As discussed by Li and Nettles [21] and Li and Uppu [22], a limitation of the existing systems is the difficulty in healing wide-opened structural-length scale crack such as cracks by impact loading. Therefore, they proposed a two-step biomimetic healing scheme – close then heal (CTH), i.e., narrow/close the wide-opened crack through confined expansion of the shape memory polymer (SMP) matrix before the molecularly-scale healing by dispersed thermoplastic particles. Rodriguez et al. [23] also proposed a similar concept based on a blend system consisting of cross-linked poly(ε-caprolactone) network (n-PCL) with linear poly(ε-caprolactone) (L-PCL) interpenetrating the network, which exhibited a combination of shape memory response from the network component and self-healing capacity from the linear component. Recently, this CTH idea has been further extended to healing cracks in conventional thermosetting polymer composites [24,25]. It mimics the healing of human skin, i.e., for a wide or deep cut, the skin needs to be first closed by stitch before new cells grow. In this idea, SMPF grid skeleton is embedded into conventional thermosetting polymer matrix as built-in suture to close crack; thermoplastic particles are dispersed in the thermosetting polymer matrix as new cells to heal crack molecularly. The idea works in such a way: when a wide-opened crack is created, heating leads to constrained shrinkage of the SMPFs, resulting in closure of the crack. Further heating leads to melting of the embedded thermoplastic particles. The molten thermoplastic is sucked into the narrowed crack through capillary force, diffused into the fractured thermosetting polymer matrix by concentration gradient, and glued the fractured surfaces molecularly when the thermoplastic wedge is solidified by cooling below the melting temperature of the

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thermoplastic particles. In addition to partial miscibility between the SMPFs/matrix and thermoplastic particles/matrix, the fundamental requirement is that $T_c < T_t < T_b < T_m < T_f$, where T_c, T_t, T_b, T_m, and T_f are respectively the curing temperature of the matrix, shape recovery temperature of the SMPFs, bonding temperature of the thermoplastic particles, melting temperature of the SMPFs, and temperature for the matrix to catch fire.

According to the biomimetic CTH mechanism, the ability for the SMPFs to close wide-opened crack depends on the recovery force applied to the two sides of the crack. Usually, as-spun SMPFs, which have very limited molecule alignment during the manufacturing process, have very small recovery stress (less than 2 MPa) [26], which may not be sufficient to close wide-opened cracks. It has been found that strain hardening through cold-drawing programming can increase the recovery stress of thermoplastic SMPs [27–29]. It has also been found that cold-compression programming or 3-D confined programming of thermosetting SMPs can also increase the recovery stress [22,30]. Therefore, strain hardening through cold-drawing programming of thermoplastic SMPFs may enhance the healing efficiency of the proposed system. It is noted that, as discussed by Li and Shojaei [24], it is impractical to heat an entire structure with large size in order to activate the constrained shape recovery of the embedded SMPFs and to heal a crack somewhere within the structure, for instance a crack in the fuselage of an aircraft. Ideally, heating should be localized and surround the cracked region, i.e., "hot" in the cracked region and "cold" in the remaining of the structure. However, it is not clear if local heating can heal a wide opened crack or not as the entire panel was heated in [25]. The purpose of this study is thus to investigate (1) the level of cold-drawing on the healing efficiency of a thermosetting polymer composite embedded with thermoplastic SMPFs and thermoplastic particles and (2) the possibility of healing wide opened crack by localized heating surrounding the cracked region.

2. Experimentation

2.1. Raw materials

EPON™ Resin 828, an undiluted clear difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin, and D.E.H. 24 curing agent by Dow Chemical were used to prepare the thermosetting polymer matrix. This is a low temperature curing polymer which can avoid shape recovery of the embedded SMPFs during the curing process. According to the manufacturer, the cured epoxy has a tensile strength of 69 MPa and modulus of elasticity of 2750 MPa.

CAPA 6506 by Perstorp UK Limited, a high molecular weight linear polyester derived from caprolactone monomer, was used as the thermoplastic healing agent. It is a white powder with a molecular weight of 50,000. The density of the particle is 1.1 g/cm^3, the melting temperature is 58–60 °C, and 98% of the powders have a particle size of less than 0.6 mm.

The same SMPFs used by Li et al. [25] were used in this study. They were polyurethane fibers manufactured by a melt spinning process. The polyurethane was synthesized using poly(butylene adipate) (PBA) (Sigma-Aldrich, USA), 4'4-diphenylmethane diisocyanate (MDI) (Sigma–Aldrich, USA) and 1,4-butanediol (BDO) (Sigma–Aldrich, USA) with PBA as the soft segment phase and (MDI + BDO) as the hard segment phase. Dibutyltin dilaurate was used as catalyst with a content of 0.02 wt%. The molecular weight of PBA is about $M_n = 650$. The average formula weight ratio was (MDI + BDO): PBA = 1021: 300. Based on the formula weight ratio, the segmented SMPFs have about 77% by weight of hard segment domain and about 23% by weight of soft segment domain. Fig. 1 shows an SEM image of one individual fiber by JEOL JSM − 6390 scanning electron microscope.

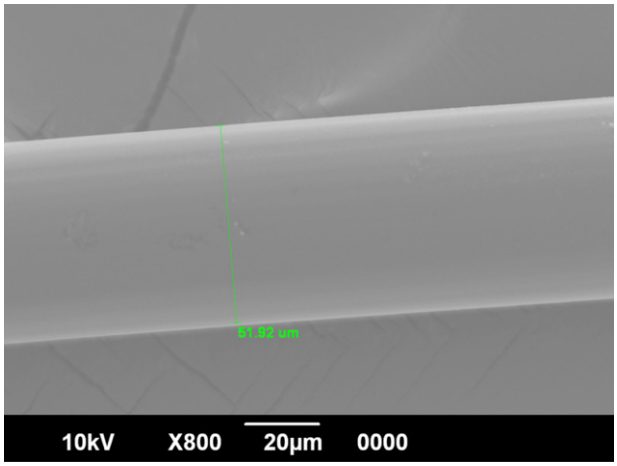

Fig. 1. SEM image of a single SMPF (the diameter of the fiber is 51.92 μm).

2.2. Determination of fiber volume fraction

In order to evaluate the effect of fiber strain hardening on the healing efficiency, it is required that the embedded fiber be able to close a crack with given width. Obviously, this depends on both fiber volume fraction and recovery stress. To this purpose, beam specimens with an artificial crack were prepared. A beam specimen embedded with SMPF bundles is schematically shown in Fig. 2(a). At the center of the beam, there exists a through-thickness crack with width of 2w. The pre-cracked beam is clamped at both ends during healing process. The reason of using clamped boundary condition is to simulate localized heating of the cracked beam specimens. In this condition, the heated beam represents "hot" region in a large structure and the clamped boundary condition simulates the constraint by the remaining "cold" portion of the entire structure. The fiber volume fraction required for SMPFs without strain hardening (which has limited molecule alignment during manufacturing) to close the central crack can be found by simple stress analysis.

Based on a rudimentary stress analysis, the half crack width is related to the recovery force of the fiber strands as given below:

$$w = \int_0^l \frac{F_r}{abE(x)}\mathrm{d}x \tag{1}$$

where F_r is the recovery force by the fiber bundles, which is equal to $nA\sigma_r$, in which n is the number of fibers, A is the cross-sectional area of each fiber, and σ_r is the recovery stress of the fiber. $E(x)$ is the modulus of elasticity of the polymer matrix at the fiber recovery temperature. l, a and b are the half length, width and thickness of the beam, respectively.

Assuming $E(x)$ is a constant (uniform temperature along the beam) and σ_r is also a constant, the above equation can be rewritten as:

$$w = \frac{nA\sigma_r l}{abE} \tag{2}$$

For the polyurethane SMP fibers used in this study, the recovery stress of the as-spun SMPF is about 2.0 MPa [25]. The modulus of the EPON 828 epoxy at 80 °C, which is the proposed healing temperature in this study, is about 200 MPa. The diameter of the fiber as seen from the SEM image in Fig. 1 is about 0.05 mm. If the beam specimen to be used during healing efficiency tests has a gage