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Enhanced adhesive strength between shape memory polymer nanocomposite and titanium alloy

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ABSTRACT

Due to their unique shape memory capability, shape memory materials have been studied in numerous areas that require shape reconfiguration. This capability enables the adaptive wing structural concept. The structure prototype required enhanced interfacial strength between the shape memory polymer composite and structural metal alloys to enable the use of the shape memory polymer composite in this application. The interfacial adhesion properties between the shape memory polymer composite and a titanium alloy were systematically investigated. Surface modification of the titanium alloy with silane coupling agents improved the adhesion strength. The shape memory polymer was toughened using amphiphilic poly(n-butylene oxide)-b-poly(ethylene oxide) and with carbon nanotubes. The toughened shape memory polymer composite showed enhanced adhesion strength compared to the non-toughened system. Toughened shape memory polymer with both 5 wt% poly(n-butylene oxide)-b-poly(ethylene oxide) and 2 wt% carbon nanotube against surface-modified titanium alloy showed up to 113.5% increase in the adhesion strength, compared to the control. To investigate the adhesion mechanism, the adhesive fracture surface was investigated by tracking the locus of failure using high-resolution electron microscopy and energy dispersive X-ray spectroscopy.

1. Introduction

Shape memory materials (SMMs) have drawn tremendous interest due to their unique shape memory capability to be contorted from a permanent shape to a sustained temporary shape, until recovery to the permanent shape is supplied by an external stimulus [1,2]. SMMs also possess other unusual properties such as a drastic change in elastic modulus, large recoverable stroke/strain, and adaptive characteristics. These unique characteristics of SMMs can enable various applications such as smart fabrics, intelligent medical devices, self-deployable space structures, morphing structures and packaging. Compared to metallic or ceramic shape memory materials, shape memory polymers (SMPs) have superior, intrinsically-high elastic deformation, broad tailorability of mechanical properties by molecular design, potential biocompatibility and biodegradability, ductility, low weight and ease of processing [3,4].

Polyurethane (PU)-based SMPs and epoxy-based thermosetting SMPs are the most popular among SMPs [5,6]. Epoxy-based SMPs have relatively high mechanical strength and high transformation temperatures compared to polyurethane-based SMPs. There have been many efforts to improve the properties of SMPs and to expand applications for this material class. Gall and his co-workers incorporated silicon carbide fibers to increase the recovery force generated by a SMP. Constrained bending recovery force was shown to increase by 50% with the addition of 20% silicon carbide fibers [6]. Koerner and his coworkers demonstrated remote actuation of a SMP composite. A CNT filled PU-based SMP was activated by infrared irradiation or electric current [7]. Several studies have been published that demonstrate progress toward morphing aircraft structures. SMPs have been used to change wing span, chord length and sweep [8,9] to reduce aerodynamic drag. In a recent effort to use SMPs in an aircraft structural component that requires repeated retraction and deployment [10], however, it was determined that SMPs alone do not provide sufficient mechanical ntegrity. While titanium alloy may possess the mechanical

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properties to be used in this application, the actuation load is too high for practical operational use. However, a SMP composite laminated with titanium alloy layer of appropriate thickness can show both great shape memory effect and mechanical durability. These complementary characteristics of SMP's shape memory property and titanium alloy's high mechanical durability can support the application. Advancing this concept required the development of approaches to enhance the interfacial strength between SMPs and titanium alloys. Such increased adhesive strength can be greatly beneficial in other situations where a SMP must be joined to a metallic structure.

In this work, the interfacial adhesion between a SMP and a titanium alloy were systematically investigated. This study includes an examination of the effect of CNTs, amphiphilic diblock copolymer and silane coupling agents on the adhesive strength between a SMP and a titanium alloy.

2. Materials and methods

2.1. Materials

Bisphenol A diglycidyl ether, (3-glycidyloxypropyl)trimethoxysilane (GPTS) and (3-aminopropyl)trimethoxysilane (APTS) were purchased from Aldrich Chemical Co. and were used without further purification. 3,4′-oxydianiline was purchased from Mitsui Petrochemical, Ind., and used without further purification. Multiwall carbon nanotubes (MWCNT) were obtained from Duke University and used in the as-received condition. Poly(n-butylene oxide)-b-poly(ethylene oxide) (PBO-PEO diblock copolymer (PBE)) was obtained from Dow Chemical and was used as a toughening agent without further purification. Titanium alloy coupons (Ti beta 21S, ASTM B265 grade 21, 1.6 mm thick) were purchased from Titanium Metals Corporation.

2.2. Synthesis and preparation of specimens

Epoxy-based thermosetting shape memory polymer (SMP) resin was synthesized with bisphenol A diglycidyl ether as a resin and amines as the curing agent. The molar ratio of epoxide equivalent to amines was 1:1. The precursors were mechanically premixed and a predetermined amount of CNT or PBE was added to the resin. The premixed resin was placed in a mixing apparatus consisting of a temperature-controlled sonication bath and a mechanical stirrer. The resin was mixed under high shear at 60 °C and 25 kHz sonication for 2 h.

Lap-shear test specimens consisting of titanium alloy adherends and the SMP as the adhesive were prepared and tested according to ASTM D5868-01. Each pair of titanium alloy coupons was mechanically abraded by grit-blasting (Trinc Dry Blast Model 36/PP, Trinity tool company, 0.48–0.52 MPa; Flex-O-Lite grade particle, 100–170 mesh (US nominal)), and cleaned using an acid mixture ($HF:HNO_3:H_2O = 5:45:50$ v/v) for about 5 min and rinsed with water and isopropanol to generate a fresh oxide layer on the surface. Control samples, without any adhesion promoter, were prepared with the SMP resin between two titanium alloy coupons that were cleaned as described above. The lap-shear specimens were clamped under pressure of about 30 kPa and cured in a convection oven at 125 °C for 4 h, 150 °C for 4 h and 175 °C for 2 h. To enhance adhesive strength, some of the cleaned titanium alloy coupons were further chemically treated with silane coupling agents; (3-glycidyloxypropyl)trimethoxysilane (GPTS) or (3-aminopropyl)trimethoxysilane (APTS) (Fig. 1(a) and (b)). The process for silane coupling agent treatment was as follows (Fig. 1(c)): First, a predetermined amount of GPTS or APTS was dissolved in acetic acid aqueous solution with pH of 4.5 for hydrolysis of methoxy groups. The methoxy groups of the silane coupling agent were hydrolyzed in water, and silanetriol formed as a consequence of the reaction [11]. The concentrations of GPTS or APTS were 0.05, 0.1, 0.5 or 1 wt%. The titanium alloy coupons were immersed in the GPTS (or APTS) solution under agitation at room temperature for 30 min. The GPTS- (or APTS-) modified, titanium alloy coupons were placed in a convection oven at 100–120 °C for 30–120 min for the condensation reaction of the silanol groups with the titanium alloy surface. The SMP resin was then applied to the surface treated, titanium alloy coupons, as mentioned above, to prepare the lap-shear specimens.

2.3. Characterization

The surface (interfacial) energies of the titanium alloy and the SMP were measured with a dynamic contact angle tensiometer (Data Physics DCAT 21). Dynamic contact angles were measured by dipping specimens into liquid at a constant velocity of 0.2 mm/s to a depth of 5 mm below the liquid surface using a Wilhelmy plate method:

$$F = mg + P\gamma_l \cos\theta - F_b \tag{1}$$

where F is the measured total force, m is the specimen mass, g is the acceleration of gravity, P is the specimen perimeter, γ_l is the surface energy of the liquid, θ is the contact angle and F_b is the buoyancy force. The contact angle for this procedure was taken as the advancing contact angle, θ_A. Then, the receding angle, θ_R was measured as the specimen was pulled out of the liquid at a rate of 0.2 mm/s. The Young's thermodynamic equilibrium angle, θ_E, was assumed as shown in Eq. (2) [12,15].

$$\cos\theta_E = (\cos\theta_A + \cos\theta_R)/2 \tag{2}$$

The relationship between the surface (interfacial) energy and the measured contact angle can be expressed by the Young's Eq. (3) and a geometric-mean method (4) and (5):

$$\gamma_{lv}\cos\theta_E = \gamma_{sv} - \gamma_{sl} \tag{3}$$

$$\gamma = \gamma^d + \gamma^p \tag{4}$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d + \gamma_l^d} + \sqrt{\gamma_s^p + \gamma_l^p}\right) \tag{5}$$

where γ_{lv}, γ_{sv} and γ_{sl} represent the surface energy of the liquid in equilibrium with its saturated vapor, the surface energy of the solid in equilibrium with its saturated vapor and the interfacial energy between the solid and the liquid. γ, γ^d and γ^p represent the total surface energy, dispersive component and polar component, respectively. Subscripts l and s represent the reference liquid and solid titanium alloy specimen, respectively. Here, we used two reference liquids, water (γ = 72.8 mN/m; γ^d = 21.8 mN/m; γ^p = 51.0 mN/m) and glycerol (γ = 64.0 mN/m; γ^d = 34.0 mN/m; γ^p = 30.0 mN/m), to calculate the surface energies of the titanium alloy [12–15]. The interfacial energy between the titanium alloy and the SMP resin was calculated from the measured surface energy of the titanium alloy and the contact angle of SMP resin on the titanium alloy specimen using the Young's equation [12].

Surface roughness of the specimens was characterized using a profilometer (Fries Research & Technology GmbH, Model FRT MicroProf® 100). Adhesion tests were performed at room temperature using a universal test machine (UTM, Instron, Model TTCM1) equipped with a 22,241 N (5000 lbf) load cell. The test machine was operated in stroke control with a crosshead speed of 0.127 cm/min, according to ASTM D 1002. Critical stress intensity factors (K_{IC}) of resin and composite specimens were evaluated at room temperature using a Micro-Tester (Instron, Model 5848)