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Mimicking mussel adhesion to improve interfacial properties in composites

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ABSTRACT

The macroscale properties of polymer–matrix composites depend immensely on the quality of the interaction between the reinforcement phase and the bulk polymer. This work presents a method to improve the interfacial adhesion between metal–oxides and a polymer matrix by performing surface-initiated polymerization (SIP) by way of a biomimetic initiator. The initiator was modeled after 3,4-dihydroxy-L-phenylalanine (dopa), an amino acid that is highly concentrated in mussel foot adhesive proteins. Mechanical pull out tests of NiTi and Ti–6Al–4V wires from poly (methyl methacrylate) (PMMA) were performed to directly test the interfacial adhesion. These tests demonstrated improvements in maximum interfacial shear stress of 116% for SIP-modified NiTi wires and 60% for SIP-modified Ti–6Al–4V wires over unmodified specimens. Polymer chain growth from the metal oxides was validated using X-ray photoemission spectroscopy (XPS), ellipsometry, scanning electron microscopy (SEM), and contact angle analysis.

1. Introduction

In this paper, we aim to demonstrate a dramatic improvement in adhesion between a metal–oxide and a surrounding polymer by performing surface-initiated polymerization (SIP) using a biomimetic initiator. While the properties of a composite depend on the properties of the constituents (for example carbon fibers and epoxy), the quality of the interaction between the phases critically determines performance [1,2]. Strong interfaces are necessary for efficient load transfer to the reinforcement phase to increase the stiffness of the composite [2–4]. For improved toughness, the interfacial adhesion should be high but still allow for some energy dissipation through debonding [5]. Therefore, optimizing the interfacial properties between different phases is an important factor in designing composites with maximum load transfer and increased strength and toughness.

There are a host of reinforcing materials, such as metals, silica, and carbon nanotubes that could be utilized to increase the strength and stiffness of a polymer. One especially interesting possibility for reinforcement is NiTi due to its unique properties: the shape memory effect (SME) and pseudoelasticity (PE) [3]. These effects result from a diffusionless phase transformation between an austenitic and martensitic crystallographic structure in response to heating and cooling or mechanical deformation. When starting in the martensitic regime, shape memory alloys (SMA) can be deformed but then return to their original shape after heating induces an austenite phase transformation. If originally in the austenitic regime, PE materials can be strained up to 8% and fully recover their original shape upon unloading [6]. These recoverable deformations are far beyond a typical metal's yield point of 0.02%. Researchers hope to capitalize on these properties to create smart materials such as thermo-mechanical actuators [3,7–9], self-healing composites [10], and impact and creep resistance structures [11]. In such applications of SMA composites, maximum interfacial adhesion is necessary to effectively transfer the load from the matrix to the filler.

It is especially important to optimize the interfacial properties in nanocomposites as the reinforcing phase has an extremely high surface area to volume ratio [4]. In nanocomposites, an interphase zone with structure and properties different than those of the bulk polymer naturally surrounds each nano-sized particle [12,13]. The ultimate goal of modifying the surface of the nano-sized particles is to improve the particle-matrix coupling characteristics of the interphase zone while simultaneously preventing particle–particle aggregation [14]. If these two objectives are satisfied, the properties of the entire composite can be transformed with small additions of nano-sized particles.

One of the simplest methods to increase interfacial adhesion in composites is to increase the surface roughness of the reinforcement phase by sandblasting [3]. The increased roughness will lead to

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mechanical interlocking during pull out. While this method is simple to perform on large reinforcements, it cannot be performed when the reinforcement phase is on the same size-scale or smaller than grains of sand. Another method to increase the interfacial adhesion between metal oxides and polymers is through the use of silane coupling agents. Silane coupling agents have one Si group that interacts with various inorganic surfaces and another group that reacts with organic materials. This strategy is widely used in dental composites to increase the interaction between the reinforcement phase and the polymer host [15]. However, researchers have found that the stability of silane coupling agents (Ti–O–Si and Zr–O–Si) in aqueous environments is low [16]. Consequently, if metal–oxides are to be used as reinforcements in biomedical or structural applications where water is present, there is a need for interfacial adhesions that remain robust in aqueous environments allowing for proper stress transfer and longer-lasting mechanical integrity.

For the purpose of creating a surface modification technique that is stable in aqueous environments, we approached interfacial design from a biomimetic perspective. By incorporating chemical constituents found in adhesive proteins secreted by mussels, we designed an initiator for surface-initiated polymerization [17] and demonstrated its use on TiO_2 nanoparticles [18].

Marine mussels, like *Mytilus edulis*, use a natural adhesive to adhere to virtually any surface even in the presence of waves and tides [19,20]. Researchers have been unable to synthesize an adhesive as strong, versatile, and unaffected by water as the mussel's glue. The unusual amino acid dopa makes up 20 mol% of the *M. edulis* foot protein-3 [21] and 26 mol% of foot protein-5 [22] that are found at the substrate–pad interface. A single dopa molecule was found to bind reversibly to TiO_2 surfaces with a dissociation force of 805 pN in the presence of water [23]. To put 805 pN in perspective, single molecule atomic force microscopy (AFM) experiments revealed a dissociation force of 2000 pN for the silicon–carbon covalent bond [24] and approximately 10–20 pN for the unzipping of DNA hydrogen bond pairs [25]. Therefore, the dopa–titania interaction of 805 pN is quite strong and robust in aqueous environments making it an attractive candidate to emulate in efforts to improve the adhesion in inorganic–polymer composites.

In this paper, we demonstrate that our dopa-initiator is as effective as silane coupling agents in improving interfacial adhesion in inorganic–polymer composites. We grafted PMMA polymer coatings from NiTi and Ti–6Al–4V wires by SIP using our dopa-mimetic initiator. As TiO_2 is found abundantly on NiTi oxide surfaces, dopa should also bind well to NiTi substrates [26]. We then quantified the improvement in interfacial adhesive properties between the SIP-modified alloy wires and polymer systems by performing single fiber pull out experiments of the wires embedded in a PMMA matrix. By pulling out a fiber embedded in another material, one can quantify the interfacial properties of the system by examining the relationship between peak load and embedded length. In short fiber or nanoreinforced composites, every particle intersecting a fracture plane is essentially subjected to a fiber pull out test during fracture. Macroscale fiber pull out tests offer an indication of this reinforcement behavior. At the nanoscale, the surface modification should have an even more dramatic effect on the interfacial properties due to the larger surface area to volume ratio. Therefore, a measure of the improvement in interfacial adhesion from our fiber pull out tests not only characterizes the adhesive behavior of macroscale composites, but also has implications for the reinforcement-ability of TiO_2-containing nanoparticles in polymer nanocomposites.

2. Experimental

2.1. Materials

NiTi (55% Ni, 45% Ti) and Ti–6Al–4V (Grade 5, alloy of 6% aluminum and 4% vanadium, extra low interstitials) wires with a diameter of 0.127 mm were purchased from Small Parts, Inc. (Miami Lakes, Florida). For flat, reference substrates, silicon wafers were coated with a 20 nm-thick layer of TiO_2 (99.9% pure, West Cerac,

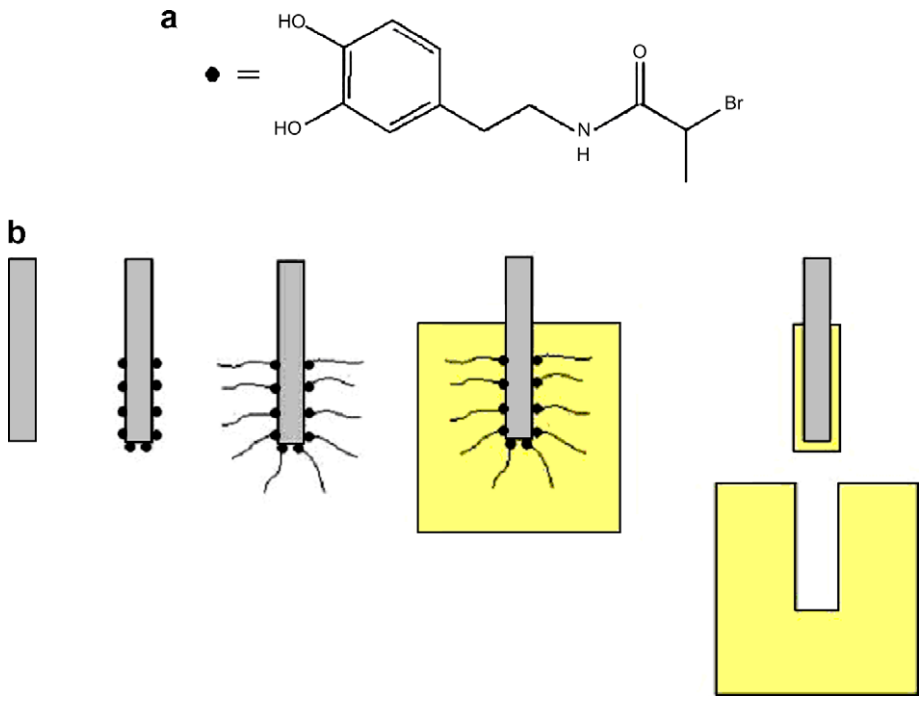

Fig. 1. (a) Chemical structure of dopa-mimetic initiator. The catechol end of the initiator reacts strongly and reversibly with metal–oxide surfaces while the bromine terminus is available for SIP via atom transfer radical polymerization (ATRP). (b) Schematic of the experimental steps including clean wires, immobilized initiator, SIP from initiator, wires embedded into PMMA matrix, and wires pulled out from bulk PMMA.