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Torsional properties of helix-reinforced composites fabricated by magnetic freeze casting

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ABSTRACT

Helix-reinforced structures are found in a variety of natural materials, from the helical architecture of the narwhal tusk to the Bouligand structures in the exoskeletons of crustaceans. Drawing inspiration from these natural structures, a novel materials processing method, known as magnetic freeze casting, is used to fabricate helix-reinforced hybrid composites. The ZrO_2–epoxy composites investigated here exhibit enhanced torsional properties due their helical architectural organization. In torsion, the maximum tensile and compressive stresses induced by a state of pure shear are oriented at ±45° to the axis of rotation. As a result, the composites with helix-reinforcement oriented parallel to the direction of maximum compressive stress (at ~45°) exhibit the highest shear moduli. Bioinspired, hybrid composites with helix-reinforced structures may be useful for a variety of engineering applications, from the cylindrical shafts in combustion engines to golf clubs and bone implants.

1. Introduction

Helices are found in a variety of natural structures [1], such as the stems of woody plants [2], the skeletons of silica sponges [3], and the tusks of narwhals [4]. These naturally occurring structures grow in response to external stresses and provide reinforcement against induced torsion. Similarly, the double-helix structure of DNA governs its torsional rigidity, an important property that determines its superhelix, tertiary structure [5]. Unlike spirals that have a continuously increasing radius of curvature, such as those commonly found in mollusk shells [6,7] and the horns and antlers of many ruminant mammals [8], helices have a constant radius of curvature and propagate along a central axis [1]. The growth, morphology, and mechanical advantage of spirals and helices observed in natural structures have fascinated scientists for decades [1,9]. Skalak et al. [10] and Harary and Tal [11] developed mathematical models to describe, respectively, the surface growth and morphology of several biological ultrastructures, such seashells, horns, and antlers. At the microstructural level, another form of the helix present in many natural materials is the twisted-plywood or Bouligand structure [12]. This helicoidal structure has been observed in the exoskeletons of crustaceans [13–15] and the scales of fish [16,17]. Recently, it was reported that the twisted nature of the fibrous layers in these materials is mechanically advantageous, enhancing their impact resistance and fracture toughness [15,17].

In modern architectural design, both spirals and helices appear in a variety of synthetic structures, primarily for their natural beauty. However, the helix is also an efficient mechanical design that provides an optimal distribution of stresses in structures subjected to torsional loading (e.g., torsion springs) [18]. Drawing inspiration from this natural design principle, engineering materials that are subjected to external torques may benefit from similar helix-reinforced architectures. Few attempts to utilize the helix for enhanced torsional rigidity in synthetic materials have been reported. Apichattrabrut and Ravi-Chandar [19] and Cheng et al. [20] fabricated helicoidal fiber-reinforced composites that exhibited improved damage tolerance in response to tension, bending, and impact. However, the torsional rigidity of the composites was not investigated [19,20]. Several patents [21–25] on helical reinforced materials have been filed as well. However, to the best of our knowledge, only the torsion transmitting glass shaft

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invented by Rodgers and Howald [25] utilizes helix-reinforced architectures to improve the torsional rigidity of cylindrical shafts.

Recently, Porter et al. [26] invented a novel materials processing method, known as magnetic freeze casting, to fabricate ceramic scaffolds with helical architectures. This technique expands on conventional freeze casting – a popular method in which a colloidal suspension, typically composed of ceramic particles and water, is directionally frozen, then sublimated to remove the frozen solvent, and sintered to partially densify and strengthen the porous constructs [27,28]. During solidification, the particles are pushed between and trapped within growing ice crystals, leading to lamellar pore channels that are direct replicas of the frozen solvent [27,28]. Subsequently, the porous ceramics can be infiltrated with polymers or metals [29–32], yielding hybrid composites with hierarchical architectures that mimic the natural features of bone (e.g., osteons) or abalone nacre (e.g., brick-and-mortar structures). Although many freeze cast materials exhibit high strength and toughness [29,32], these properties are generally limited to a single direction - parallel to the direction of ice growth.

Magnetic freeze casting uses magnetic fields to manipulate magnetic nanoparticles (i.e., Fe_3O_4) during solidification. This process steers ceramic particles in the direction of the magnetic flux path. Previously, this method was shown to enhance the compressive strength and stiffness of ceramic scaffolds perpendicular to the direction of ice growth, parallel to an applied magnetic field [26]. The enhanced compressive properties obtained are due to the microstructural alignment of lamellar walls in two perpendicular directions: (1) the ice growth direction and (2) the magnetic field direction. In the same study [26], several cylindrical scaffolds with helical architectures were fabricated by rotating magnetic fields about the solidification direction. These scaffolds exhibited biphasic material properties. A circumferential helix composed of a higher-density, Fe_3O_4-rich phase surrounded an interior lower-density, Fe_3O_4-poor phase. The helix was composed of dense lamellar walls aligned parallel to the direction of the prevailing magnetic field. It was proposed that this helical architecture may act as a reinforcing structure, enhancing the torsional rigidity or shear modulus of the material [26,28].

We show herein, both experimentally and analytically, that these helical architectures enhance the torsional rigidity of magnetic freeze cast composites. To do this, it is necessary to compare the shear modulus of composites having identical material compositions, with and without helical architectures. Although several shear test methods currently exist [33,34], the solid-rod torsion test was selected for this work [35]. Previous investigations show that the torsion test is best suited to induce a state of pure shear stress in cylindrical composite samples [35,36]. The method predicts both the shear strength and stiffness of a material from a single test [35,36]. In addition, torsion testing minimizes local material and stress concentration effects as well as unwanted bending moments due to slight misalignments of the samples [35,36]. Experimental measurements of the torsional rigidity (i.e., shear modulus) versus the angle of helix-reinforcement were compared to determine an optimal angle of reinforcement.

2. Materials and methods

2.1. Magnetic freeze casting

Helix-reinforced composite samples were prepared using a custom built freeze cast unit and rotating permanent magnet as previously described [26]. Aqueous slurries of 10 vol.% or 20 vol.% ZrO_2 powders (Sigma Aldrich, St. Louis, MO), with an average diameter of 0.2–0.5 μm, were mixed with 3 wt% (of the total solids) Fe_3O_4 nanoparticles (Sigma Aldrich, St. Louis, MO), with an average diameter of ~50 nm, and 1 wt% of each: organic binders, polyethylene glycol (PEG) (Alfa Aesar, Ward Hill, MA) and polyvinyl alcohol (PVA) (Alfa Aesar, Ward Hill, MA), and an ammonium polymethacrylate anionic dispersant, Darvan® 811 (R.T. Vanderbilt Company, Inc., Norwalk, CT). The slurries were ball milled in an alumina grinding medium for 24 h, followed by degassing under low vacuum for 10–20 min. Approximately 3 mL of the degassed slurries were poured into a polyethylene mold with a 9 mm inner diameter and frozen at a constant rate of 10 °C/min. During solidification, a magnetic field of 0.12 T was rotated about the ice growth direction (*Z*-axis) at 0.05 rpm, 0.20 rpm, or 0.40 rpm, resulting in the helix-reinforced architectures. After freezing, the samples were removed from the mold and lyophilized in a bench-top freeze dryer (Labconco, Kansas City, MO) at −50 °C and 350 Pa for 72 h. The porous green constructs were then sintered in an open air furnace for 3 h at 1300 °C with heating and cooling rates of ±2 °C/min.

Following the sintering process, the porous scaffolds were infiltrated with epoxy (EpoxiCure Resin, Buehler, Lake Bluff, IL), resulting in ceramic–polymer composites with varying volume fractions and angles of helix-reinforcement. To infiltrate the scaffolds, the two-part epoxy solution was first mixed thoroughly for 2–3 min. Then, the porous scaffolds were immersed in the liquid epoxy solution and subjected to a low vacuum for 30 min to degas the solution and infiltrate the scaffolds. After complete infiltration, the wet samples were removed from the liquid epoxy and set at room temperature for 24 h, allowing the epoxy to harden and cure. For clarity, even though the ceramic phase of all the composites contains 3 wt.% Fe_3O_4, it is simply referred to as ZrO_2 throughout this study.

2.2. Material characterization

Scanning electron microscopy (SEM) images were taken at 15 kV on a Philips XL30 field emission environmental scanning electron microscope (FEI-XL30, FEI Company, Hillsboro, OR). For SEM preparation the samples were sputter-coated with iridium using an Emitech K575X sputter coater (Quorum Technologies Ltd., West Sussex, UK).

The thicknesses and angles of helix-reinforcement and the relative volume fractions of the ZrO_2 and epoxy phases of the composites were measured from optical images and scanning electron micrographs using ImageJ software (National Institutes of Health, Bethesda, MD). The helices were measured from optical images using the segment and angle measurements tools. The relative volume fractions were measured from the cross-sections of the composites, where the thresholds of SEM images were adjusted equally to measure the % area of each phase. Four different locations across each cross-section were measured to determine the distribution of densities caused by the rotating magnetic fields.

X-ray diffraction (XRD) was performed on a D2 Phaser X-ray diffraction tool (Bruker AXS, Madison, WI). XRD experiments confirmed that the crystal structure of the ZrO_2 phase remained monoclinic before and after sintering, while a small portion of the Fe_3O_4 phase transformed from magnetite (Fe_3O_4) before sintering to hematite (Fe_2O_3) after sintering at 1300 °C. No apparent transformation due to interactions between the ZrO_2 and Fe_3O_4 phases was observed.

2.3. Torsion testing

The torsional properties of the ZrO_2–epoxy composites with varying volume fractions and different angles of helix-reinforcement were compared using the solid-rod torsion test. The torsion tests were performed on a custom built torsion testing device, capable of twisting the cylindrical composites to induce a state of pure shear stress (see Appendix A).