Introduction

Past experiments have already proven that silk, a natural protein produced by silkworms and spiders, exhibit intriguing physical properties such as exceptionally high moduli and toughness. Silk fibroins (SF) can be further reconstituted into ultrathin (<100 nm) films while retaining most of these properties for a wide variety of bioapplications. These ultrathin films can be further enhanced by incorporating materials with them to create nanocomposites; in particular, addition of graphene oxide (GO) can increase the ultimate stress the film can take up to about 200%. But not affecting ultimate strain. Hence, the goal of this research was to improve the ultimate strain by adding dopamine (DA) to the SF-GO nanocomposite.

Procedure

The silk was harvested from cocoons of the silkworm Bombyx mori. To dissolve the glue-like sericin, the silk was boiled in a sodium carbonate solution for 30 minutes, rinsed repeatedly for about 10 times, and weighed. It was then left to dry until an ideal 23% weight loss was achieved. To break down the actual filaments, a 20% w/v solution of 9.3 M lithium bromide was used for 1 hour at 65 °C. Afterwards, the LiBr was dialyzed using a 10,000 MWC dialysis cassette submerged in 2 L of water, which was replaced every hour and left overnight. The silk solution was then centrifuged for 20 mins at 9000 rpm and 5 °C twice. The collected supernatant was then diluted to 0.2% for use.

GO solutions were obtained by exfoliating graphite sheets through successive sonication and centrifugation, known as the Hummers Method.

The general protocol was to first spin-cast a sacrificial layer of polystyrene (PS) dissolved in toluene on the wafer, then alternately spin-cast SF sand GO solutions until the ideal thickness of about 50 nm was reached. To determine the completion of the spincasting phase, an estimate of the film’s thickness was obtained using an ellipsometer, and later confirmed by AFM. Small samples of the film were obtained by cutting a grid of about 2mm x 2mm onto the wafer. By submerging the wafer under water, the hydrophobicity of PS would cause the films to float on the water surface, allowing them to be caught onto TEM copper grids with a 150 μm radius. The sacrificial layer of PS was dissolved by dipping the copper grids into toluene, and the quality of the films were inspected using an optical microscope.

Slight changes to this protocol were observed in functionalizing SF with DA. Appropriate weights of dopamine hydrochloride were mixed with the 0.2% SF solution to obtain 1:4 and 1:8 ratios between SF and DA. DA was polymerized by submerging the film under a pH=10 buffer for at least 2 hours, but at different times: after spincasting and dissolution of toluene; after spincasting and before dissolution of toluene; and prior to spincasting (SF, DA, and the buffer were mixed in one vial).

The physical properties of the films were determined using buckling and bulging tests. A greater emphasis was placed on the bulging test, as it is more comprehensive (uniaxial compression vs biaxial compression) and provides the complete stress-strain curve.

Results and Discussion

Initial morphology checks for nonpolymerized dopamine functionalized SF-GO nanocomposites proved to be promising. Silk molecules were observed to have a uniform coverage, as well as denser adhesion to the GO flakes (Fig 1). Most films also had uniform appearance on the microscopic level as well. Only samples whose PS layer was dissolved before polymerization only proved to be defective, as the films were observed to be already broken upon inspection with the optical microscope. We suspect that the film is too thin (without PS layer, film is around 2/3 thinner) to handle the harsh polymerization process.

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References