Tribology of Spider silk-Polymer Composite

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1. INTRODUCTION

UHMWPE is a linear polyethylene that has an extremely high molecular weight. Some of its properties include a tremendously high impact resistance, a self-lubricating and nonstick surface, excellent chemical resistance to most solvents, superior low-temperature properties, outstanding sound damping and energy absorption characteristics and electrically insulating and dielectric properties. In comparison with High Density Polyethylene (HDPE), UHMWPE is significantly more abrasion-resistant and wear-resistant[1].

While UHMWPE has been modified using carbon fibers and hot isostatic pressing, there have been no accounts of UHMWPE being processed in combination with spider silk fiber. Spider silk, or more specifically, spider dragline silk is a high performance fiber with mechanical properties rivaling that of the best man-made materials[2-4]. Spider silk is a composite material with hierarchical structure. It is made up primarily of amino acids, whereby glycine, alanine, glutamine and arginine are the most abundant and comprise of 74% of the total amino acids present[5]. In particular, spider dragline silk has been thought to be composed of mainly two proteins, Spidroin I and II[6,7]. Studies have also revealed that spider dragline silk undergoes what is termed as supercontraction in the presence of water, in which the dragline silk experiences a very large axial shrinkage when wetted[8,9].

This project attempts to fabricate a composite of spider silk and polymer via direct compression moulding and conduct a series of tests to determine its engineering properties. This report will focus on the fabrication and tensile testing of the composite.

2. MATERIALS AND METHODS

2.1. Spiders and silk

Young adult female golden orb-web spiders of the native species *Nephila pilipes* were procured from their natural habitats and housed in well-ventilated 50 x 30 x 30cm Perspex containers. The spiders were sustained on a diet of mealworms and beetles. The spiders were first lightly anesthetized with CO_2 gas and restrained on a platform for forcible silking. Dragline silk samples were then reeled onto a cardboard ring with a drawing speed of 2 cm/s using a designed motorized setup at ambient room conditions of 22 ± 3ºC and 69 ± 2% RH. The collected silk was mounted onto paper frames to be used in composite manufacture. Single threads of the dragline silk fiber, which typically consists of two minor ampullate gland (MI) strands and two major ampullate gland (MA) strands, were also collected, wetted and restrained on small paper frames to be used for tensile tests in supercontraction studies.

2.2. Direct compression molding

A stainless steel mold (see Fig. 1) was designed to fabricate small 1.5 x 1.5 x 40mm polymer or composite samples via direct compression molding to be used for tensile tests. UHMWPE (GUR 1020, Perplas Medical Batch No. 20172M, Polymer Lot No. CM331323) powder was carefully placed in the mold cavity and the mold halves fitted together. Compression pressure was applied in the form of steel springs and blocks (see Fig. 2). Cartridge heaters of 240V, 200W swaged-in leads were used to raise mold temperature, which was controlled by a Yokogawa temperature control box and ANSI Type 'T' copper-constantan Omega® "surface-mount" thermocouple. The polymer was heated to 150ºC melting temperature and then made to undergo a recrystallization soak at 90ºC before cooling to room temperature. In composite manufacture, silk mounted on four 60 x 60 x 0.2mm paper frames was layered alternately with UHMWPE powder and then processed accordingly (see Fig. 3).

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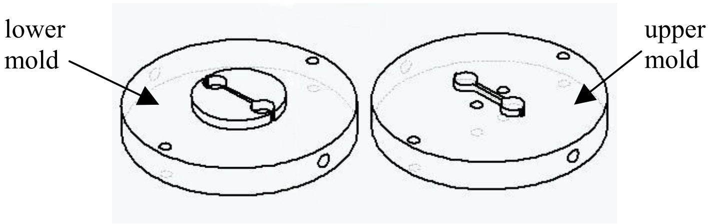

Fig.1: Stainless steel mold

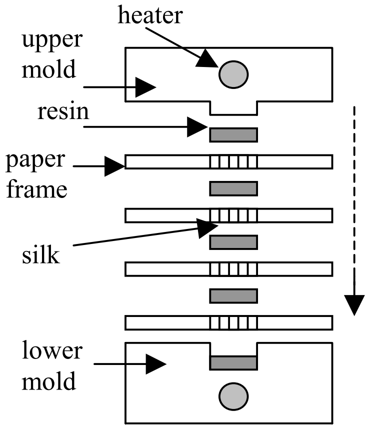

Fig. 3: Composite manufacture

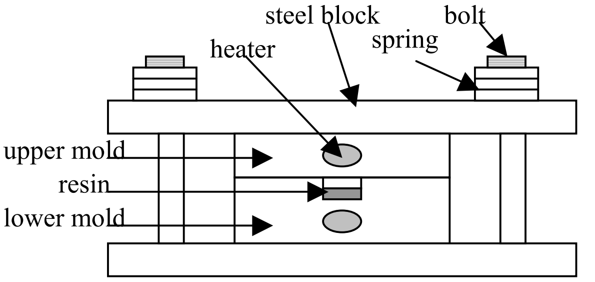

Fig. 2: Schematic of compression molding apparatus

2.3. Supercontraction testing

Individual silk fibers were soaked in water for 10, 20 and 30min. The ends of each fiber thread were cemented using a cryanoacrylic acid ester adhesive (Bostik® Superglue) onto 10 x 5 x 0.2mm plastic tabs to enable better handling. The weight of each plastic tab was measured to be 0.09g. The samples were then left to dry in ambient room conditions on a metal frame.

2.4. Tensile testing

Silk tensile tests were done on the Instron 5848 Microtester using a 2.5N load cell with 10% / sec strain rate. Wetted silk fibers were mounted on 50 x 30 x 0.2mm paper frames using superglue. Each paper frame was gripped by manual grips and the paper edges cut off. The fiber gauge length was 30mm. The fiber was examined with an optical microscope to ensure that there were four MA and MI strands. Polymer and composite tensile tests were done using a 1kN load cell with 0.5mm/min tensile extension. Each sample was meticulously examined for macro defects before mounting between pneumatic grips. The gauge length was 18mm. The sample ends were affixed to cardboard with adhesive to prevent slippage during tensile testing. All tests were carried out under ambient room conditions.

2.5. Scanning Electron Microscopy

Silk samples were gold coated in a sputter coater using 15mA current and 6Pa vacuum pressure for 40s duration and their diameters measured in a JEOL JSM-5600LV SEM with an acceleration voltage of 15 kV. SEM photomicrographs were taken at working distances of 12-15mm.

3. RESULTS AND DISCUSSION

3.1. Silk fiber supercontraction

10 silk fiber samples were measured for their initial lengths, immersed in water for 10 min and then dried in air. Their supercontracted lengths were then measured again. The process was repeated for 20 and 30min. The % reduction in lengths for the samples were calculated and shown in Table 1. Tensile tests were subsequently conducted on the samples mounted on paper frames.

	% reduction in length		
sample	10 min soak	20min soak	30min soak
average	37.25	34.25	35.95

Table 1: % reduction in sample lengths

There appears to be no direct correlation between soaking time period with % reduction in length. The silk samples were observed to have supercontracted by 30-40% of their original lengths. This was lesser than the amount of supercontraction reported in past studies for a similar species of spider *Nephila clavipes* in previous studies[8, 9].

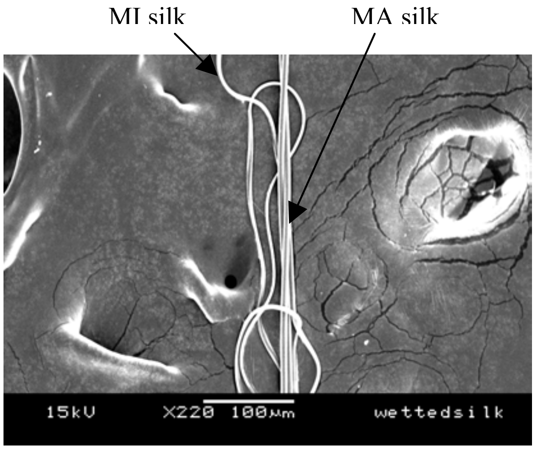

Fig. 4: Wetted silk x220 magnification

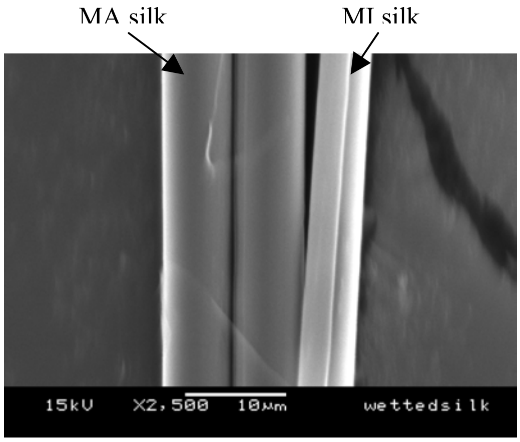

Fig. 5: Wetted silk x2500 magnification

Fig. 4 and 5 show wetted silk at x 220 and x2500 magnification respectively. It was observed that the MI silk formed loose curls around the MA silk in tension. It was apparent that only the MA silk supercontracted while the MI silk remained largely unaffected. This was consistent with findings from previous works[8,9]. The tensile stresses and strains of the supercontracted silk vary over a range of values due to the biological nature of the silk. There appears to be no obvious correlation between tensile stress/tensile strain with soak time period. However, supercontracted silk exhibit lower tensile stress and greater % breaking elongation as compared to normal silk.

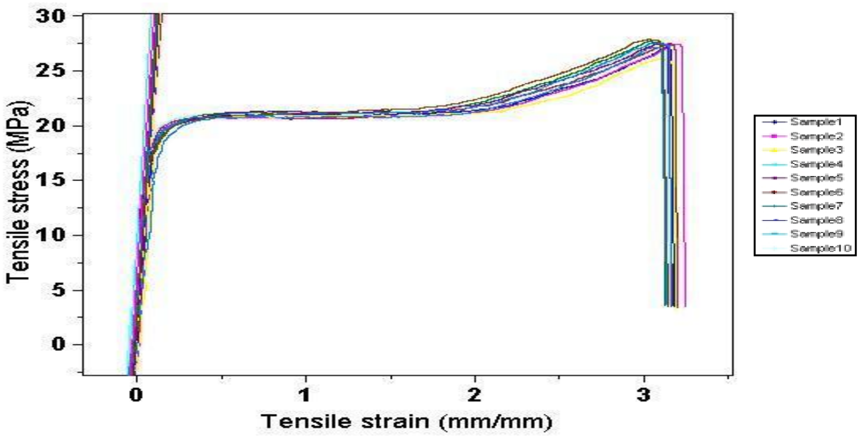

Fig. 6: Stress-strain graph for UHMWPE

3.2 Polymer/composite tensile testing

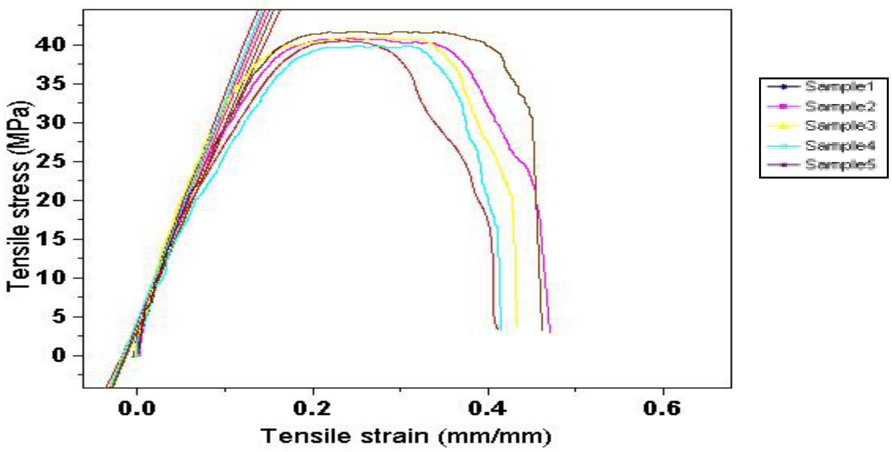

Fig. 7: Stress-strain graph for composite

The UHMWPE stress-strain graph for 10 samples (see Fig. 6) is characterized by an initial peak load, followed by a membrane drawing phase in equibiaxial tension, which shows strong molecular weight dependence[1].

The composite stress-strain graph (see Fig. 7) is limited to only 5 samples due to limited silk supply. The graphs are not very consistent, possibly due to poor bonding between polymer matrix and silk fiber. However, the composite samples were observed to have relatively higher tensile stress of approximately 40MPa as compared to 26MPa of polymer samples. Also, tensile strains for the composite samples were observed to be much lower than that of polymer samples but this is again probably due to poor interfacial bonding between matrix and fiber. The SEM photomicrograph of the composite cross-section reveals poor interfacial bonding between fiber and matrix (Fig. 8).

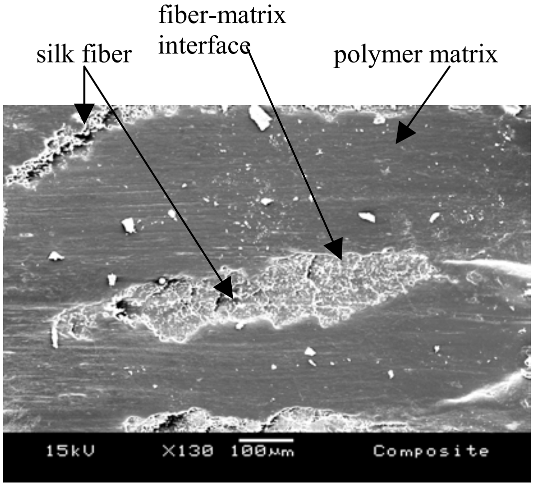

Fig. 8: Composite cross-section x130 magnification

4. CONCLUSION

The supercontraction properties of *Nephila pilipes* spider silk was studied and found to be relatively consistent with previous work[8, 9], although the supercontraction observed was lesser. Tensile testing of the UHMWPE samples produced results that were consistent with studies by Kurtz[1]. However, composite tensile testing did not produce good results although it was observed that the composite samples had consistently higher tensile stresses than the polymer samples. It was deduced that the poor composite tensile test results were due to poor interfacial bonding between fiber and matrix. It is believed that better composite fabrication, such that good interfacial bonding is achieved, will yield more satisfactory results. Also, this project used biological or natural silk which has properties that vary over a wide range and are affected by spider and environmental conditions[10]. Finally, it is hoped that a superior quality spider silk-polymer composite can be fabricated in the near future.

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