# PREPARATION OF CARBON NANOTUBE-SILK COMPOSITE

A Senior Scholars Thesis

by

SUNDEEP SHARMA

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

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Major: Biomedical Engineering

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Approved by:

Research Advisor: Mustafa Akbulut
Director for Honors and Undergraduate Research: Sumana Datta

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# ABSTRACT

Preparation of Carbon Nanotube-Silk Composite. (April 2011)

Sundeep Sharma
Department of Biomedical Engineering
Texas A&M University

Research Advisor: Dr. Mustafa Akbulut
Department of Chemical Engineering

A composite is made up of two distinct materials and the resulted properties are different from the individual precursors. Composite combines a huge or bulkier element called matrix and reinforcement called filler or fiber. Fiber is added in the matrix to increase the stiffness of the matrix and enhance or alter its physical properties. Since silk has high levels of toughness, strength and multifunctional nature, we decided to use bombyx mori as a matrix. Because of the superior mechanical properties, i.e., high tensile moduli, and strength of carbon nanotube, we chose carbon nanotube as a reinforcement fiber to enhance the mechanical properties of resulting composite. The main issue encountered while preparing composite was to fully disperse individual nanotubes in the matrices, because nanotubes tend to form clusters and bundles. Hence, we used ionic liquids to dissolve the cocoon, and processed homogenization of FCNT with silk by sonication, stirring. For testing, different weight percentages of functionalized carbon nanotube were used as a filler to make the silk composite, and nanoindentation and tensile tester tested the samples. The composite of various concentrations did not show the expected result of increasing mechanical properties with decreased carbon nanotube concentration. Hence, it

was concluded that a different method to functionalize carbon nanotube should be implemented.

# DEDICATION

Dedicated to my beloved Dad, Mr. Deepak Raj Sharma, and Mom, Radhika Sharma, and brother, Sudeep Sharma.

# ACKNOWLEDGMENTS

I am greatly thankful to all the individuals who inspired and helped me to carry out this research. I want to thank the Department of Chemical Engineering for giving me an opportunity to extend my knowledge by doing research and also for letting me use the departmental data and equipment. I am deeply grateful to my supervisor, Dr. Mustafa Akbulut, and mentor, Anna Chen, from Texas A&M University whose suggestion and encouragement aided me to continue the research and gave me encouragement to learn about my research topic. I am also deeply thankful to my lab colleagues, Ming, Vinay and Bassem, for their support. Especially, I would like to give my special thanks to my dear friends, Nishedh Khanal, Binod Karki, and Maheshwor KC, for their encouragement and support that helped me continue my research.

# NOMENCLATURE

| | |
|---|---|
| CNT | Carbon Nanotube |
| MWCNT | Multiwalled Carbon Nanotube |
| FCNT | Functionalized Carbon Nanotube |
| HATU | 2-(1H-7-Azabenzotriazol-1-yl)--1,1,3,3-tetramethyl uronium hexafluorophosphate Methanaminium |
| $SOCl_2$ | Thionyl Chloride |
| MWNT-COCl | Acyl Chloride |
| LMCS | Low Molecular Weight Chitosan |
| DMF | Dimethylformamide |
| BMIMCl | 1-Butyl-3-methylimidazolium Chloride |
| BMIMBr | 1-Butyl-3-methylimidazolium Chloride |
| LiCl | Lithium Chloride |

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# CHAPTER I

# INTRODUCTION

In recent years, preparing composites has been the main focus for many researchers. A composite is made up of two distinct materials and the resulting product properties are different from the individual precursors. Composite combines a huge or bulkier element called the matrix and reinforcement called filler or fiber. Basically, a fiber is added in the matrix to increase the stiffness of the matrix and enhance or alter its physical properties.[1] Composite ranges from polymer matrix composites, metal matrix composites to ceramic matrix composites. In polymer matrix composites, polymers are the matrix component and the filler may be carbon, or glass, depending on the properties of the composite needed. In my research, I used silk as a polymer and carbon nanotube as filler. Similar kinds of research have been conducted with spider silk. The extraordinary toughness of spider silk was five times higher than the same weight steel wire and also has inspired bio-based commercialization efforts.[2] Currently, scientists are trying to make the similar mechanical properties of silk using synthetic materials.

Carbon nanotubes are allotropes of carbon and a nanocylindrical structure. Since carbon nanotubes possesses high flexibility, low mass density, and large aspect ratio

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This thesis follows the style of *Journal of Royal Society of Chemistry*.

these properties make carbon nanotube metallic and semi conducting.[3] Because of its mechanical and electrical properties, it is also used as a filler agent. There are lots of experiments conducted to transfer carbon nanotube on polymer. But the filler agent on bombyx mori silk is the first experiment conducted. The main issue for transferring carbon nanotube to polymer is the chemical affinity of carbon nanotube towards the polymer. Therefore, covalent bond is preferred for polymer composite to get the ideal properties for composite.

Besides chemical affinity, homogeneity is also an issue. If a composite is not properly homogenized, the stress transfer from carbon nanotubes to the polymer lesser exists. To make the silk composite homogenized, ionic liquids are also needed to dissolve the cocoon. Carbon nanotube is modified to make a composite with the polymer and the modification can be either non-covalent or covalent. Non-covalent modification is physical adsorption or wrapping of polymers to the surface of carbon nanotube.[1] Another way of modification is covalent modification where the chemical bond is established between Carbon nanotube and polymer. In my research, I am functionalizing carbon nanotubes by covalent attaching proteins to CNT surface using various methods.

The polymer used in the experiment is the cocoon which is derived in the pupal stage of bombyx mori. Bombyx mori cocoon consists of two proteins fibroin and sericin. Fibroin protein is the central structure of the silk and the sericin protein is the sticky material surrounding the fibroin. The scientists are trying to make the similar mechanical

properties of silk using synthetic materials.[2] Nothing has been discovered yet. Therefore, our experiment will be also trying to make the composite of bombyx mori silk and carbon nanotube to enhance the mechanical properties of the resulting composite.

# CHAPTER II

# METHODS

Various processes for preparing silk composites are employed throughout the length of my research. For the first part of my research, carbon nanotube was functionalized through various processes. After functionalization, carbon nanotube was introduced with the silk. The second part of the research included the dissolving of cocoon with the ionic liquids and the homogenization of silk and carbon nanotube.

## Covalent functionalization of SWCNT

The Process includes the oxidation of carbon nanotube and functionalization of carbon nanotube with ethylenediamine.

### *Oxidation of carbon nanotube*

A mixture of concentrated sulfuric acid and nitric acid were sonicated in a ratio of 3:1 with SWCNT at 40 degrees Celsius to add carboxylic acid functional group on the SWCNT surface. [4] The mixture was added drop wise to distilled water and then filtered through a 10μm polycarbonate paper. After washing the mixture with DI water, the mixture was dried in a vacuum over at 40 °C.

Covalent functionalization of CNT with ethylenediamine[4]

Oxidized CNT was sonicated with ethylenediamine for dispersion. Again the resulting mixture was sonicated with mixing HATU. After sonication, the mixture was diluted with methanol and filtered using 10μm pore size polycarbonate filter paper. Finally, the mixture was washed extensively with excessive methanol to get the functionalization of CNT with the functional group amine.

Covalent Functionalization of MWCNT with LMCS[5]

Another approach of functionalization of CNT was carried out. For the first step of this process, the reflux of acid mixture was done for 24h resulting MWNT-COOH. Acid mixture was the mixture of Concentrated Sulfuric acid and Nitric acid in a ratio of 3:1. The oxidized MWNTs in $SOCl_2$ together with DMF were refluxed for 48h to convert the CNT bound functional group carboxylic acids into acyl chloride. The dried LMCS and LiCl were dispersed in DMF, heated to 120 °C, and stirred under dried Nitrogen for 2h. The resulting MWNT-COCl was added to the cooled LMCS and DMF mixture and also pyridine. The mixture was sonicated, stirred, and refluxed under nitrogen for 48h. After cooling the mixture, it was filtered through a 0.2 μm pore size Teflon, and dried. The resulting black solid was stirred in distilled water for 5h, and was filtered through a 0.2 μm pore size Teflon. The residue was sonicated in water for 1 h, filtered, washed with DI water, and extracted with water in a Soxhlet apparatus for 72h. The final product was dried under vacuum.

**Preparation of composite**

0.6 g BMIMCl, 2.8 g BMIMBr, FCNT (1% of silk) and 0.1 g of silk were homogenized properly. The homogenization process includes 1 h of sonication and 24 h of stirring under heat. The resulted mixture was filtered with ethanol followed by water and dried under vacuum for 24 h.

# CHAPTER III

# RESULTS

## Composite preparation from FCNT with ethylenediamine

Various weight percentages of FCNT was used to make a composite to determine the hardness and elastic modulus. We tested; 0.1 wt % of FCNT, 0.01 wt % of FCNT with the cocoon. The effect of indentation load, in terms of contact depth on the hardness for composites of different weight percentage of FCNT is shown in Fig.1. To make our test better, the composite was also prepared with the regenerated cocoon. Nanoindentation result for hardness shows the decrease in concentration increases the hardness whereas regenerated cocoon composite has higher hardness relative to others as shown in Fig.1. It is noticed that 0.1 wt % of FCNT filler, does not shows any change in hardness on nanoindentation test.

Nanoindentation test for elastic modulus also shows the increase in elastic modulus with decrease in concentration. As similar to hardness test, elastic modulus of the 0.1 wt % of FCNT filler remains constant.

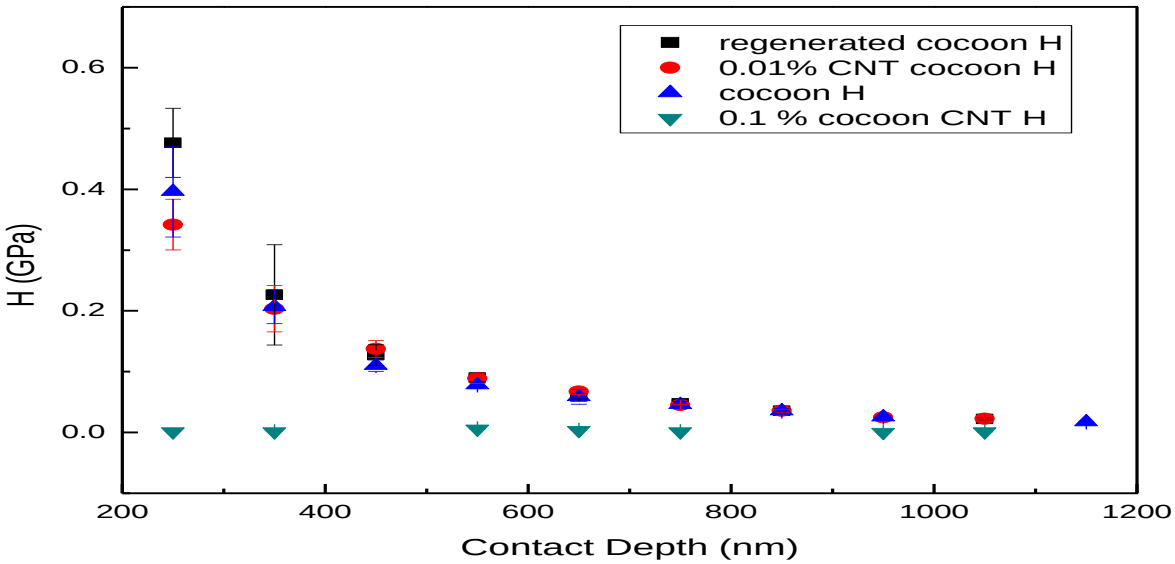


**Fig. 1**: Hardness summary collected from nanoindentation

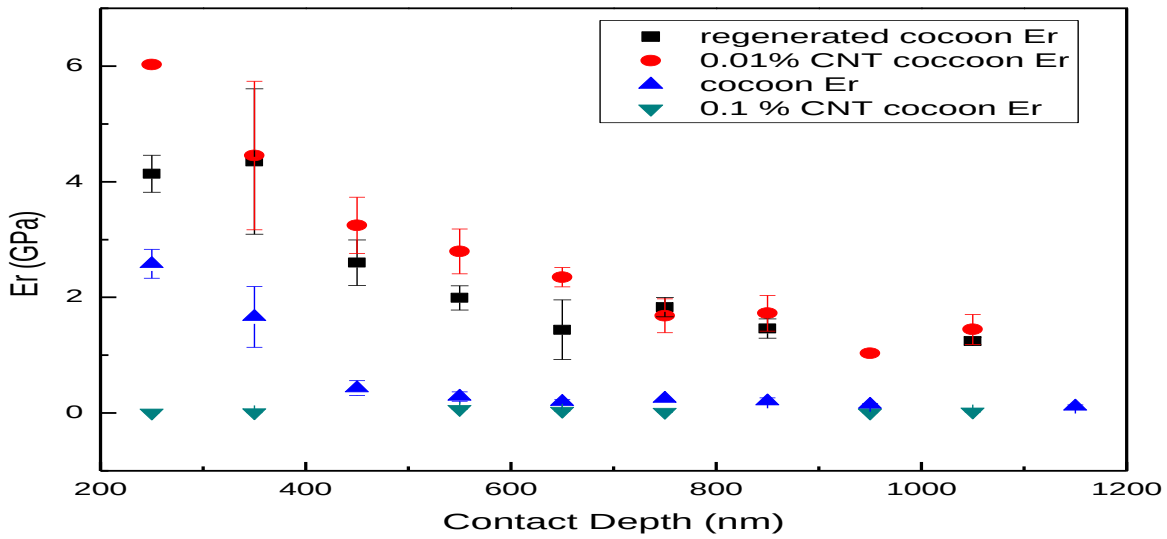


**Fig. 2**: Elastic modulus summary collected from nanoindentation

**Composite preparation from FCNT with LMCS**

The composite were made of 1.5 wt % FCNT, 0.5 wt % FCNT, and 1.5 wt % FCNT filler for tensile test. As shown in Table 1, with the change in concentration of composite, tensile test does not show any trend of increase or decrease in tensile stress, tensile strain, or modulus. The unexpected result is due to the issues on homogenization and functionalization.

**Table 1**: Result collected from Tensile Testing

| | Maximum (N) | Tensile Stress (GPa) | Tensile Strain (%) | Modulus (GPa) |
|---|---|---|---|---|
| 1.5 wt% | 2.3 | 0.00017 | 11.10 | 0.0039 |
| 1 wt% | 2.99 | 0.00013 | 32.34 | 0.0024 |
| 0.5 wt% | 10.49 | 0.00054 | 20.17 | 0.0096 |

# CHAPTER IV

# SUMMARY AND CONCLUSIONS

The main goal of research was to find the composite that shows increase in mechanical properties with the increase in concentration of composite. Results from nanoindentation shows that the composite made from FCNT with ethylenediamine increase the hardness with the decrease in concentration, whereas elastic modulus of composite also increases with the decrease in concentration differing from our goal of increase in mechanical properties with increase in concentration. After not getting the result with the FCNT with ethylenediamine, composite was made by the FCNT with a low molecular weight Chitosan. Result of tensile test for different concentration of composite made from FCNT with low molecular weight Chitosan does not follow any trend of increasing of increasing or decreasing of mechanical properties with the increase in concentration of composite. Homogenization and functionalization were the main issues of not getting the desired result. FCNT was also not dispersed properly on the silk, which is another issue for not getting the expected result. Now, I am using different method for functionalizing carbon nanotube.

# REFERENCES


1. Spitalsky, Z., D. Tasis, D., Papagelis, K. and Galiotis, C. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science* 2009 **35**(3): 357-401.

2. Dalton, A. B., Collins, S., Razal, J., Munoz, E., Ebron, V.H., Kim, B.G., Coleman, J.N., Ferraris, J.P. and Baughman, R.H.. Continuous carbon nanotube composite fibers: properties, potential applications, and problems. *Journal of Materials Chemistry* 2004 **14**(1): 1-3.

3. Ajayan, P. M. and J. M. Tour. "Materials science - Nanotube composites. *Nature* 2007 **447**: 1066-1068.

4. Ramanathan, T., Fisher, F.T., Ruoff, R.S. and Brisnon, L.C. Amino-functionalized carbon nanotubes for binding to polymers and biological Systems. *Chemistry of Materials* 2005 **17**: 1290-95.

5. Ke, Gang,. Guan, Wenchao., Tang, Changyu., Guan, Wenjie., Zeng, Danlin., and Deng, Feng. Covalent functionalization of multiwalled carbon nanotubes with a low molecular weight chitosan. *Biomacromolecules* 2007 **8**(2): 322-26.

# CONTACT INFORMATION


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| Name: | Sundeep Sharma |
| Professional Address: | c/o Dr. Mustafa Akbulut<br>Department of Chemical Engineering<br>230 Jack E. Brown Building<br>Texas A&M University<br>3122 TAMU<br>College Station, TX 77843 |
| Email Address: | sunmoonsharma@tamu.edu |
| Education: | B.S., Biomedical Engineering<br>Minor: Math<br>Texas A&M University, December 2011<br>Undergraduate Research Scholar |