

# Morphological Consequence of Sonication on Lignin-CNT-Epoxy Composite

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## ABSTRACT

This project will utilize SEM and molecular modeling analysis to determine morphological consequences of sonication time on lignin particle size and the joint sonication of lignin with CNT during prefabrication. The investigation will yield a more fundamental understanding of the interactions between lignin and CNT. Currently, lignin provides a significant increase in mechanical strength to buckypaper. This study provides structural analysis to support the role of lignin in improving the mechanical properties of buckypaper. Additionally, this study will provide a pathway to greater details regarding improvements in mechanical strength and possibly other properties of the modified buckypaper.

**Keywords:** dispersion, sonication, CNT, biopolymer, lignin, SEM

## 1 INTRODUCTION

Nanotechnology promises high performance electronic and optical materials, which should revolutionize electronic and energy systems. Of nanomaterials, fullerenes are of the most highly studied [1]. Within, this project, carbon nanotubes will be used as composite fillers to increase the mechanical, and electronic properties of various electronic materials.

The addition of nanotubes in a uniform fashion has been shown to increase the electronic properties, mechanical strength and thermal properties of nanocomposites. [1] Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces. [2]

The dispersion of carbon nanotubes has been proven to be a difficult process. [4] Presently, there are several methods to increase the quality of dispersion among carbon nanotubes. [1,3,4,] Direct mixing/solution casting, melt blending, buckypaper/resin infiltration and in-situ polymerization are the key methods researchers have used to improve dispersion. In addition, factors such as; the use of surfactants, functionalization of CNT, and ultrasonication are used to enhance dispersion. [5, 6, 7, 8]

Chemical modification and functionalization has been shown to be effective in improving the solubility and dispersion of nanotubes. Additionally, functionalized nanotubes can provide bonding sites to the polymer matrix so that the load can be transferred to the nanotubes to prevent separation between the polymer surfaces and nanotubes. [5] Functionalized materials has been shown to improve the mechanical properties of nanoparticles. Zhu, showed a 30% increase in modulus and 18% increase in tensile strength indicating a well dispersed epoxy composite.[5]

The use of surfactants by Gong et al., [6] was used as a wetting agent to improve dispersion which also enhanced both mechanical and thermal properties of the nanotube epoxy composites. However, the use of acetone by Sean et al., [9] as a surfactant, showed no improvement in the modulus and tensile strength. However, ultrasonication is believed to improve the dispersion of epoxy composites. Even though ultrasonication and intense stirring may improve dispersion of nanotubes; it is still difficult to break up the entangled bundles of the nanotubes. [10] Shen et al., [11] reported single-walled nanotube (SWNT) bundle size decreases due to ultrasonication dispersion aided by a surfactant.

A new buckypaper/resin infiltration method will be used to produce buckywood. The novelty is the use of lignin, a biological polymer, as a co-surfactant and a co-binder. In this study we observe the dispersion of CNT based on the sonication time of the formentioned method via Scanning Electron Microscopy (SEM). This work shows that the increase of sonication time will enhance the dispersion quality of carbon nanotubes, thus improving the composites mechanical strength.

## 2 PREPARATION OF SAMPLE

The sample preparation process for this study utilizes a modified buckypaper fabrication process. Buckypaper is produced by adding dry purified carbon nanotube product into a mortar that has a small amount of water. Once the CNT is added, it is ground with a pestle. The resulting mixture is then sonicated. Afterwards, water dissolved surfactant is added to the mixture to form a stabilized

suspension and sonicated again. The suspension is filtrated by vacuum, washed and dried to produce paper. Lastly, the buckypaper is infused with a acetone diluted resin by vacuum infiltration and is allowed to dry. The resulting composite is shown in Figure 1.

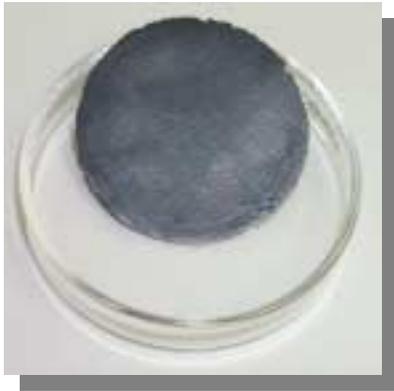


Figure 1: NBP/Epoxy composites with preformed SWNT network and good resin impregnation can reach 20~45w% SWNT loading [12]

The buckypaper process can be altered in two ways. The first method is to include lignin as a co-surfactant and sonicated as a part of the buckypaper suspension. It is important to note that only a hydrophobic form of lignin be used. The process of filtration and infiltration by resin is followed normally.

The second method is to follow the buckypaper process to just before the resin-infiltration step. Lignin is infiltrated in a water suspension. Once lignin is filtered through the sample, the resin infiltration step is resumed.

### 3 RESULTS

Figure 2 and Figure 3 shows the morphology of buckypaper under a scanning electron microscope. The micrograph shows high levels of entanglement which increases the van der Waals interaction. The nanocomposite (Figure 3) shows a fibrous mesh which resembles a marbalized system.

Although no micrographs of the modified buckypaper are available at this time, Figure 4 indicates that inclusion of lignin at a level above 30% concentration allows for a significant increase in strength. Although the results are not statistically significant, the results appear to demonstrate increased strength due to lignin incorporation. Further, it can be argued that direct incorporation has a higher impact on the final structure rather than post infiltration.

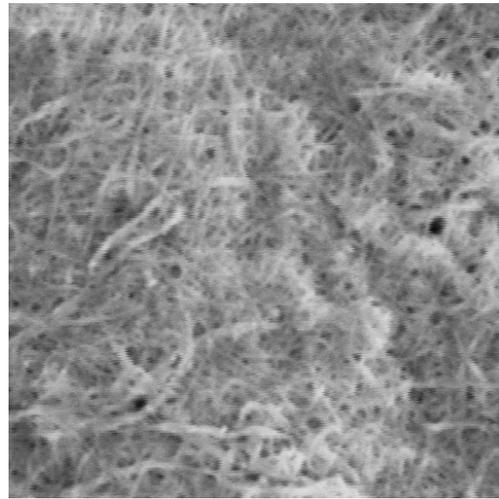


Figure 2: BUCKYPAPER - Random NBP (X 30,000) [12]

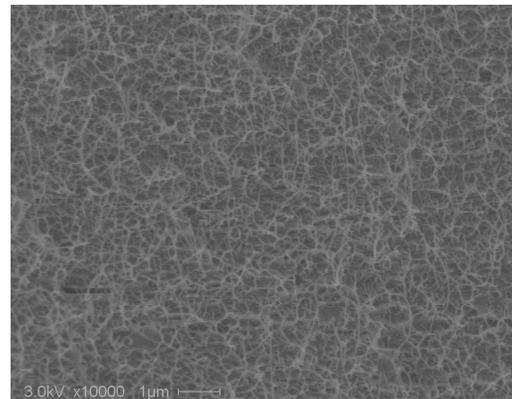


Figure 3: SEM image of the cross-section of a NBP/Epoxy composites of 43.2 w% SWNT loading [12]

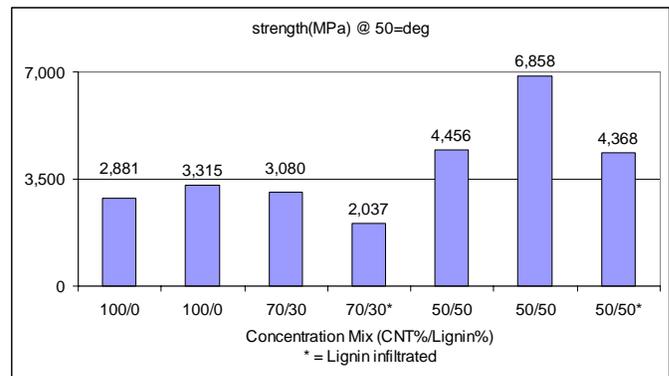


Figure 4: Observed tensile modulus in MPa at 50 degree Celcius. The X indices show the CNT to Lignin concentration. An asterisk indicates that lignin was infiltrated after the buckypaper was formed. Otherwise, the modified buckypaper was formed with lignin incorporation during the suspension stage.

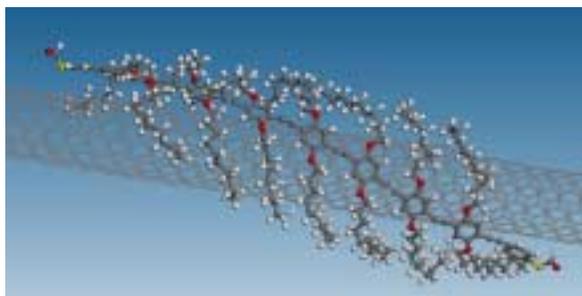


Figure 5: Molecular wrapping of a long chain molecule interacting with a section of CNT molecule. [12]

Figure 5 is a molecular model of CNT interacting with a polymer resin-like molecule. The model indicates that molecular wrapping of CNT occurs which can help to form a strong interaction between CNT and the polymer matrix. Although this observation is not novel to this experiment, it presents evidence that a lignin molecule, which generally has higher conjugation than does a cured resin molecule, can act as a bridge between the CNT and resin matrix.

#### 4 CONCLUSION

Although direct morphological conclusions cannot be made at this time, the modulus data indicates that lignin is strengthening the bulk system. Lignin particles and CNT molecules must have a high level of positive interaction. The interaction allows for either a higher level of dispersion or a scaffold for the resin molecules. A definitive conclusion; however, cannot be formed without micrographs of the lignin modified buckypaper. Albeit a definitive analysis does not exist, the data indicates that the incorporation of lignin provides a similar mechanism in the buckypaper as it does in nature as a binder. Thus, lignin should have a high affinity to CNT and the resin; thereby allowing for increase in strength through a binding bridge of the two molecular species.

#### 5 FUTURE WORK

Future studies will be conducted to better understand the dispersion within the nanocomposites. SEM, molecular modeling and further mechanical tests will be used to understand the nanostructuring that enable strength development.

#### REFERENCES

1. Zhi, Wang, Liang, Zhiyong, Wang, Ben, Zhang, Chuck, Kramer, Leslie. Processing and property investigation of single-walled carbon nanotube (SWNT) buckypaper/epoxy resin matrix nanocomposites. *Composites: Part A* 2004; Vol. 35:1225–1232.
2. Wikipedia: Carbon Nanotubes. 2006

3. Siochi, Emilie J., Working, Dennis C., Park, Cheol, Lillehei, Peter T., Rouse, Jason H., Topping, Crystal C., Bhattacharyya, Arup R., Kumar, Satish. Melt processing of SWCNT-polyimide nanocomposite fibers. *Composites: Part B*, 2004; Vol. 35: 429-446.
4. Park, Cheol, Ounaies, Zoubeida, Kent, Watson, A., Crooks, Roy E., Smith Jr., Joseph, Lowther, Sharon E., Connell, John W., Siochi, Emilie J., Harrison, Joycelyn S., St.Clair, Terry L. Dispersion of single wall carbon nanotubes by in situ polymerization under sonication. *Chemical Physics Letters* 2002; Vol. 364: 303–308.
5. Zhu, Jiang, Kim, JongDae, Peng, Haiqing, Margrave, John L., Khabashesku, Valery N., and Barrera, Enrique V. Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites through Fictionalization. *Nano Letter* 2003; Vol. 3, NUM.8: 1107-1113.
6. Gong, Xiaoyi, Liu, Jun, Baskaran, Suresh, Voise, Roger D. and Young, James. Surfactant-assisted processing of carbon nanotube/polymer composites. *Chem. Mater.* 2000; Vol.12: 1049-1052.
7. Ausman, Kevin D., Piner, Richard, Lourie, Oleg, and Ruoff, Rodney S., Korobov, Mikhail. Organic Solvent Dispersions of Single-Walled Carbon Nanotubes: Toward Solutions of Pristine Nanotubes. *J. Phys. Chem. B* 2000; Vol.104 NUM. 38.
8. Niyogi, S, Hamon, M.A., Perea, D. E., Kang, C. B., Zhao, B., Pal, S. K., Wyant, A. E., Itkis, M. E., and Haddon, R. C. Ultrasonic Dispersions of Single-Walled Carbon Nanotubes. *J. Phys. Chem. B* 2003; Vol. 107: 8799-8804.
9. Spindler-Ranta, S.; Bakis, C. E. SAMPE 2002 Symposium & Exhibition, 2002.
10. Sandler, J., Shaffer, M. S. P., Prasse, T., Bauhofer, W., Schulte, K., Windle, A. H. *Polymer* 1999; Vol. 40: 5967.
11. Shen, Kai, Curran, Seamus, Xu, Huifang, Rogelj, Snezna, Jiang, Yingbing, Dewald, James, and Pietrass, Tanja. *J. Phys. Chem. B* 2005; Vol. 109: 4455-4463
12. Data developed and shared by the Florida Advanced Center for Composite Technology