Effect of The Dissolution Method With N, N-Dimethylformamide As A Solvent On The Electrical Properties Of Acrylonitrile Butadiene Styrene And Carbon Nanotube Composites

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Abstract. The objective of this study is to create electrically conducting composite polymers using the dissolution method. Composites are made from Acrylonitrile Butadiene Styrene (ABS) as the matrix and Carbon Nanotubes (CNTs) as the filler. Composites were made using the dissolution method with N, N-Dimethylformamide (DMF). All the components were mixed then dried in a fume hood until they were formed into pellets in a compression molder. Compressed samples were optically and electrically tested. Results show that composites that were only dried in the fume hood have a bubbled structure and reach percolation around 1-5 phr. The bubbles were determined to be coming from water that got into the samples while they were drying in the fume hood. Composites were placed in a furnace at 100°C for 1 hour to take the water out of them. Results showed that furnace dried samples have a smooth surface and are more resistive than the bubbled composites. The bubbled samples were most likely less resistive than samples with a smooth surface because during the bubble formation the CNTs are being pushed closer together causing percolation to happen sooner.

1. Introduction
Electrically conducting composite polymers are important because they give the best of both worlds when it comes to polymers and conducting materials. Conducting materials are typically very dense and brittle. Polymers can give a large range of properties such as improved impact resistance, be lightweight, and yet malleable when needed. The beauty of a conducting composite polymer is that one can achieve all these properties at the same time. This allows a whole surplus of applications like; replacing metal wires were weight must be optimized, the creation of self-regulating heaters, electric noses, chemical sensors, supercapacitors for charge storage, and electromagnetic shielding materials [1-9].

In this study, Acrylonitrile Butadiene Styrene (ABS) is the polymer used to make up the matrix of the composite. ABS is an amorphous polymer which is impact resistant. It is used to make Legos [10] and is often the polymer of choice for 3D printing [11]. ABS is made from three monomers (Acrylonitrile, Butadiene, and Styrene). It has a long linear backbone with branches of polybutadiene coming out the sides. ABS is a highly resistive polymer with a resistivity of 14-16x1015 ohm.cm3, meaning it is highly insulating and does not conduct electricity [12]. Carbon Nanotubes (CNTs) are the electrically
conducting material used in this study. CNTs are very conducting with a resistivity of 2.80x10^-3 ohm.cm [13]. They are relatively small with a huge surface area and are made of only carbon atoms arranged into hybridized hexane rings [14]. There are two main types of CNTs: single-walled and multi-walled nanotubes [15]. For this study multi-walled CNTs were used.

When working with electrically conducting composites, it is important to determine their percolation threshold. Percolation occurs when there is enough of the conducting material present so that it can form a path, such that at that point the conductivity increases by several orders of magnitude [16]. The percolation threshold changes based on how the filler is dispersed in the matrix. The dispersion of the filler and the concomitant properties can be dramatically changed through different processing techniques [17]. In this study, the dissolution method is used to dissolve ABS with DMF and evenly disperse the CNT throughout the matrix.

2. Methods

2.1. Materials

Magnum ABS Resin supplied from Dow Chemical Company (Midland, Michigan), in the form of small pellets ranging in 5 mm in diameter and 2 mm in thickness. Short Multi-Wall Carbon Nanotubes, which had an outer diameter of 8-15 nm and a length of 0.5-2.0 μm, were obtained from www.cheaptubes.com HPLC grade N, N-Dimethylformamide (DMF) was supplied by VWR Chemicals.

2.2. Fabrication

Varying concentrations of ABS/CNT composites were fabricated by first dissolving the ABS in DMF. (table 1) ABS was dissolved with the assistance of a speed mixer (Flack Tek, Inc., Model DAC 150.1 FVZ-K), which mixed the solution at 2000rpm for 1-minute intervals until all the ABS was completely dissolved. Then, the CNTs were added and mixed in using the speed mixer. The solution was allowed to dry in petri dishes inside the fume hood for ~10 days. Once composites were dry, they were diced finely and then compressed in a Compression Molder Struers Prontopress-2. The Compression Molder was heated to 170°C for 15 minutes and cooled for 8 minutes with a load of 10 kN. Compressed composites had a diameter of 3.17 cm and a radius of 1.585 cm. Some diced ABS/CNT composites were also dried in a furnace (Thermolyne model 47900) before compression. Samples were heated at 100, 120, or 150°C for 1 hour before compression. After compression samples were imaged using a Pent aView optical microscope.

| phr   | wt %    |
|-------|---------|
| 0.000 | 0.000%  |
| 0.010 | 0.010%  |
| 0.250 | 0.249%  |
| 0.100 | 0.100%  |
| 0.750 | 0.744%  |
| 0.500 | 0.498%  |
| 1.000 | 0.990%  |
| 5.000 | 4.762%  |
| 10.000| 9.091%  |

2.3. Impedance measurements

Composites were coated in silver using a Denton Vacuum Desk II Turbo Sputter Coater. Then, electrical measurements were taken using a Solartron 1260 Impedance Analyzer coupled with a 1296 Solartron Dielectric Interface (Farnborough, Hampshire, England). A two-probe test set up was used and measurements were taken at frequencies from 10^3-10^7 Hz at room temperature.
3. Results and discussion

3.1. Bubbled samples

Figure 1 shows compressed ABS/CNT composite samples that were not oven-dried. These samples had concentrations ranging from 0 to 10 phr. All of these composites have a foamed structure (figure 1 (a-g)). High concentrations such as 1 phr have phase separation in some areas where CNTs visually appeared to be absent or bubble size was dramatically different in size (figure 1 (h)).

![Macroscopic pictures of samples](image1.png)

**Figure 1.** Macroscopic pictures of samples at different concentrations that all had a bubbling structure taken with the PentaView. (a) 0 phr (b) 0.01 phr (c) 0.1 phr (d) 0.5 phr (e) 1.0 phr (f) 5.0 phr (g) 10.0 phr (h) 1 phr sample that shows two different regions. The left side has a higher concentration of CNTs and larger bubbles as compared to the right side.

Figure 2 shows the electrical measurements of the bubbled samples. Percolation happens somewhere between 1 and 5 phr for the bubbled samples. The standard deviation between samples of the same concentration was approximately the same for all concentrations. This is most likely due to the samples being inhomogeneous. There is a notably large variation in resistivity between samples around percolation, this is most likely because at percolation electrical pathways are starting to form and because this process is random, more pathways can form in some samples than in others.
Figure 2. Resistivity vs CNT concentration in phr for ABS/CNT bubbled composites. Line of best fit is \( y = 8 \times 10^{11} e^{-1.644x} \). Percolation happens around 1-5 phr. 0 phr was graphed as 0.0001 phr.

3.2. The cause of the bubbles in ABS/CNT composites
Bubbling was determined to be coming from water that entered the composites while they were air drying in the fume hood. This was determined by Fourier-transform infrared spectroscopy (FT-IR). Figure 3 shows FTIR spectra for as received ABS, ABS that was dissolved in DMF and dried in the fume hood, and compressed samples. The ABS that was dissolved in DMF has a very distinctive OH bond, which is found in water. The OH stretch is absent in the compressed ABS sample indicating that the water evaporated during compression which is most likely the source of the bubbles in the compressed samples. Thermogravimetric analysis (TGA) was also used to confirm that water was the cause of the bubbles.

Figure 3. FT-IR of pure ABS, ABS dissolved in DMF and dried in the fume hood for 10 days, and ABS dissolved in DMF that had been compressed in the compression molder.

3.3. Oven drying samples before compression to eliminate the bubbling
Figure 4 shows PentaView images of diced ABS/CNT composites that were heated in a furnace at 100, 120, or 150°C for 1 hour before compression. Figure 4 (a, d, g) shows that samples that are heated at 100°C for 1 hour have the least amount of bubbles after compression. Although the 100°C treatment did not create smooth samples in ABS/CNT composite concentrations higher than 0.25 phr (figure 4 j, l, m). Samples without bubbles appeared smooth.

Figure 5 shows that heated samples were more resistive in comparison to their bubbled counterparts. The 0.01 phr sample that was heated at 100°C for 1 hour was 169.74% more resistive than the bubbled sample (figure 5 (a)) and the 0.1 phr heated sample was 87.28% more resistive than its bubbled counterpart (figure 5 (b)). This is most likely due to the bubbles pushing the CNTs closer together, causing percolation to happen sooner in the bubbled samples.

4. Conclusions
The ABS/CNT composite polymers that had a foamed structure reached percolation between 1 and 5 phr. It was determined that the foaming structure came from water that had entered the samples during heating.
processing. Water was able to be removed from the samples before compression with the use of a furnace, this process had the most success when samples were heated to 100°C for 1 hour. Heating in the furnace only worked on lower concentrations of ABS/CNT. Concentrates higher than 0.5 phr plastically deformed in the furnace at 100° C. This is most likely due to the CNTs conducting heat through the samples causing the ABS to reach its glass transition point faster and at lower temperatures. This data shows how important processing is when making electrically conducting composite polymers. By simply heating the composites before compression the resistivity and microstructure was completely changed. This means that with all the same starting materials, one could easily manipulate the properties of the composite, possibly resulting in additional potential applications for the composite. More research into the processing of these composites is needed. The furnace heated samples need to be made with a larger range of concentrations so that they can be compared more directly to the foamed composites. Also, now that it is known that water can enter the composites when they are drying in the fume hood, the time that they are allowed to air dry needs to be more strictly controlled. In future studies, experimentation with drying samples in a vacuum oven might result in more reliable results across all concentrations of ABS/CNT composites. With the vacuum oven, there is a possibility of removing the water from the samples at lower temperatures so that the plastic deformation of the high concentrated composites may be avoided. Creating and testing more concentrations around percolation should be done in the future. This way a more accurate percolation concentration can be achieved.

5. References

[1] R. Strumpfler, J. Glatz-Reichenbach (1999). Conducting Polymer Composites. Journal of Electroceramics 3[4]: 329-346.
[2] J.N. Aneli, G.E. Zaikov, O.V Mukhaniani, C. Sirghiemi, V.M. Lobo (2011). Physical Principles of the Conductivity of Electrical Conducting Polymer Composites: Review. Journal of Characterization and Development of Novel Materials 3[3/4]: 139-162.
[3] S.M. Mirvakili, I.W. Hunter (2018). Artificial Muscles: Mechanisms, Applications and Challenges. Advanced Materials 3C[6].
[4] Kai Wang, Haiping, Wu, Yuena Meng, Zhixiang Wei (2014). Conducting Polymer Nanowire Arrays for High Performance Supercapacitors. Small 10[1]: 14-31.
[5] W.E. Jones, J. Chiguma, E. Johnson, A. Pachamuthu, D. Santos (2010). Electrically and Thermally Conducting Nanocomposites for Electronic Applications. Materials 3: 1478-1496.
[6] A. Saboor, A.N. Khan, R. Jan, S. Sharif, M. Khan (2018). Mechanical, dielectric and EMI shielding response of styrene acrylonitrile, styrene acrylonitrile/polyaniline polymer blends upon incorporation of few layer graphene at low filler concentrations. Journal of Polymer Research 25: 24.
[7] GX Wang, A. Morrin, M. Li, N. Liu, XL Luo. (2018). Nanomaterials doped conducting polymers for electrochemical sensors and biosensors. Journal of Materials Chemistry B 6[25]: 4173-4190.
[8] K.M. Vighnesha, S. Sandhya, D.N. Sangeetha, M. Selvakumar (2018). Synthesis and characterization of activated carbon/conducting polymer composites electrode for supercapacitor applications. Journal of Materials Science: Mater Electronics 29: 914-921.
[9] S. Ganguly, P. Bhawal, R. Ravindren, NC Das (2018). Polymer Nanocomposites for Electromagnetic Interference Shielding: A Review. Journal of Nanoscience and Nanotechnology 18[11]: 7641-7669.
[10] WHAT LEGO® BRICKS ARE MADE FROM. (2019). Retrieved from LEGO: https://www.lego.com/en-us/service/help/bricks-building/brick-facts/what-lego-bricks-are-made-from-408100000007855
[11] ABS Filaments For Your 3D Printer. (n.d.). Retrieved from Filaments.directory: https://www.filaments.directory/en/plastics/abs
[12] S. Dul, L. Fambri and A. Pegoretti (2018). Filaments Production and Fused Deposition Modeling of ABS/Carbon Nanotube Composites. Nanomaterials 8[49]: nano8010049.
[13] WY Wang, GH Luo, J. Luo (2009). Electrical Conductivity and Thermal Properties of Acrylonitrile-Butadiene-Styrene Filled with Multwall Carbon Nanotubes. *Polymer Engineering and Science* 49[11]: 2144-2149.

[14] Guillaume Herlem, F. P. (2019). Carbon Nanotubes: Synthesis, Characterization, and Applications in Drug Delivery Systems. In *Nanocarriers for Drug Delivery Nanoscience and Nanotechnology in Drug Delivery* (pp. 469-529).

[15] James P. Schaffer, T. H. (2011). *Principles and applications- Engineering Materials Vol 1 Georgia Institute of technology, Materials science & engineering*

[16] Runqing Ou, Siddhartha Gupta, Charles Aaron Parker, Rosario A. Gerhardt (2006). Fabrication and Electrical Conductivity of Poly(methyl methacrylate) (PMMA)/Carbon Black (CB) Composites: Comparison between an Ordered Carbon Black Nanowire-Like Segregated Structure and a Randomly Dispersed Carbon Black Nanostructure. *The Journal of Physical Chemistry, 110*(45), 22365-22373.

[17] Siddhartha Gupta, Runqing Ou, Rosario A. Gerhardt (2006). Effect of the Fabrication Method on the Electrical Properties of Poly(acrylonitrile-co-butadiene-co-styrene)/Carbon Black Composites. *Journal of Electronic Materials*(2): 224-229.

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