

Intercalation of Poly-acrylonitrile (PAN) into carbon nanotubes

V. Chan

University of California at Berkeley, Berkeley, CA 94720

K. Sun, A. Yarin, and C. M. Megaridis

Mechanical & Industrial Engineering, University of Illinois at Chicago, Chicago, IL 60607

The primary goal of this work is to fill 200 nm average diameter CVD Carbon nanotubes (CNTs) with Poly-acrylonitrile (PAN) - a carbonizable polymer - with the diffusion process reported by Bazilevsky et al [1] and to control the thickness and structure of the PAN inside the CNTs. Transmission electron microscope (TEM) was used as a tool to monitor the morphology of polymer filled nanotubes. TEM images of CNTs that were filled using five different PAN concentrations of the PAN/DMF solution - 0.1, 0.5, 1, 2, and 5 wt% - demonstrated that the intercalation process is independent of the initial PAN concentration in solution. Furthermore, a DMF rinse process was used to remove polymer that was clinging to the outer walls of the CNTs, allowing clearer visual of the PAN structure in the interior of the CNTs. Finally, TEM images of filled CNTs taken through a carbonization process demonstrated that the CNT samples were able to survive the high temperature, with some damage to the CNT walls.

Introduction

The superior qualities of carbon nanotubes (CNTs) in the areas of strength and conductivity make them highly attractive for future technological applications.² A prominent area of research is the usage of carbon nanotubes as media for fluid transport. Currently, scientists are trying to incorporate nano-technology into micro-fluidic chips so that large scale biological and chemical processes can be automated in the same way calculations are automated using integrated circuits in computer chips.^{3,4} However, to exploit the use of carbon nanotubes as channels for fluid transport, it is crucial that the fundamental behavior of fluids at the nano scale is understood.⁵ Earlier, Liu *et al.*⁶ showed that CNTs can be filled with polymers using supercritical CO_2 . This demonstrated that CNTs can indeed be intercalated with polymers, but the technique was not viable because of the high pressures and low temperatures necessary to obtain supercritical CO_2 .⁶ More recently Bazilevsky *et al.*¹ demonstrated that carbon nanotubes can be filled with low molecular weight polymers through a simple diffusion process, thereby eliminating the necessity for high pressures and low temperatures.

In this paper, it is demonstrated that the same technique can also be used to fill carbon nanotubes (CNTs) with poly-acrylonitrile (PAN), a carbonizable polymer.⁷ Furthermore, the effects of DMF (a solvent that dissolves PAN) and the effects of carbonization on the filled CNT samples are explored. The overall goal of this project is to develop a method to control the thickness and structure of the PAN intercalated in the CNTs. To do this, each aspect of the intercalation process needs to be carefully analyzed. As a result, the experimental methods and results and discussion section in this paper are split up into three subsections - filling of CNTs with PAN, extent of polymer filling, and carbonization - so that each aspect

of the intercalation process can be clearly understood.

Experimental Methods

Filling CNTs with Poly-acrylonitrile (PAN)

CVD 200 nm average diameter heat treated CNTs were used in this study. These CNTs were dispersed in ethanol through manual shaking; the CNTs featured fragile walls and could not be sonicated. Polymer solutions of 0.1, 0.5, 1, 2 and 5 weight percent PAN in Dimethylformamide (DMF) (99.8%, Sigma Aldrich) were prepared by mixing PAN (Polysciences, Inc) in DMF with a stir bar at 60°C for one day. The PAN used in this experiment has a molecular weight of 150kDa. The materials used to fill the CNTs with PAN are identical to that of Bazilevsky *et al.*,¹ with the exception of the CNTs and the polymer used.

The intercalation process of PAN into the CVD CNTs is similar to that of Bazilevsky *et al.*¹ A single drop of the CNTs/ethanol suspension was dispensed on a lacey carbon transmission electron microscope (TEM) grid and allowed to dry for approximately 10 minutes. After the CNTs were dry, a single drop of the polymer solution was dispensed on the dried CNTs and was also allowed to dry. The substrate below the TEM grid is crucial to form a thin layer of polymer on top of the CNTs. A diagram of the set up can be seen in Figure 1.⁴

The samples were analyzed under a JEOL-3010 transmission electron microscope (TEM) operating at 300 kV. The TEM images revealed that the PAN completely filled the CNTs, but also showed that there was an excess of polymer wrapped around the exterior of the CNTs. To clear up the excess polymer for better visualization of the interior polymer structure, a rinsing method using DMF was introduced. The PAN filled CNTs were rinsed by

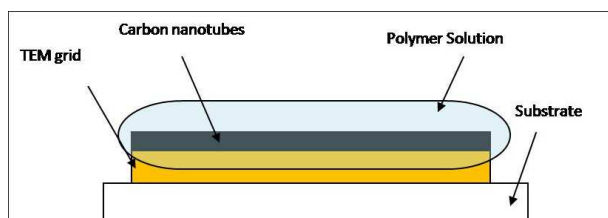


FIG. 1: Experimental set up for intercalation of PAN in CVD CNTs.

submerging in DMF at 60°C for 1 hour.

It is important to note that the PAN within the CNTs needs to be completely dry before the rinsing can be performed. If the PAN is still wet, the rinsing step will completely wash out the PAN, leaving behind empty CNTs. To ensure that the PAN within the CNTs is dry, the filled CNTs were either left out to air dry for 24 hours or placed in an oven at around 50°C for 2 to 3 hours.

Extent of polymer filling

The rinsing technique used to remove PAN from the outer wall of the CNTs (as described earlier) can also be used to remove the polymer from within the CNTs, because the deposit material inside and outside is identical. The only difference between the inside and the outside is the transport rate of DMF; DMF is readily available to dissolve the PAN on the outside, but needs to diffuse into the CNTs to dissolve the PAN trapped inside. Therefore, rinsing the PAN filled CNTs for an extended period of time should eventually dissolve the polymer within the CNTs as well.

It is expected that the DMF dissolves the PAN from the openings of the CNTs towards the center of the CNTs as a function of time and temperature. Therefore, by changing time and temperature of the DMF rinse, different thicknesses of polymer filling should be possible.

To compare the effect of concentration on the extent of PAN filling in the CNTs, intercalation of 0.1, 0.5, 1, 2, and 5 wt% PAN/DMF solutions were used.

To compare the effect of DMF rinsing time, 0.5 wt% PAN solution filled CNTs were rinsed at 80°C for 2, 5, and 21 hours.

Carbonization

PAN was chosen because it is known to be a carbonizable polymer and would therefore allow porous structure formation within the CNTs after the carbonization process. A porous structure can lead to many immediate applications, such as a nano-sieve, which can be used to separate particles of different sizes at the nano-scale as demonstrated in Figure 2.

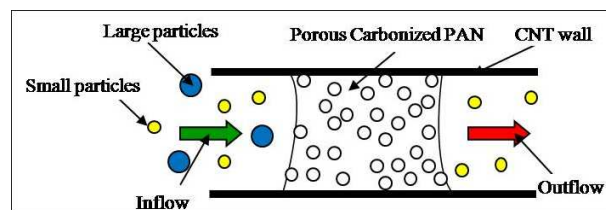


FIG. 2: Nano-Sieve. The large particles in the inflow are filtered out. As a result, the outflow contains only the small particles.

The carbonization process is performed by placing the samples, prepared by the method discussed earlier, into a 47900 Barnstead Thermolyne Furnace. The samples are first heated to 250°C and held there for 30 minutes so that all the impurities in the samples can be oxidized away. After 30 minutes at 250°C, the samples are ramped in a nitrogen purge at 5°C per minute until 750°C. When the sample reaches 750°C, it is held there for 1 hour before it is allowed to cool down to room temperature.

By heating the polymer to such high temperatures, the volatiles within the polymer are burned off, leaving only the carbon structure behind. A nitrogen purge is necessary so that the remaining carbon does not oxidize away at the elevated temperatures.

For the carbonization step, DuraSiN Mesh TEM grids (Protochips, USA) were used. These grids are silicon nitride based and are capable of withstanding temperatures of up to 1000 °C. The TEM grid used contains holes of 7 μ m and spacing between the holes of 2 μ m.

Results and Discussion

Filling CNTs with PAN

The TEM images in Figure 3 demonstrate that PAN can be readily intercalated into CNTs by a simple diffusion process. The PAN structure seen inside the CNTs is not identical to the foam, dispersed bubble, or peapod polymer structure as described in Bazilevsky *et al.*,¹ and instead exhibits a rough, solid pockmarked structure.

The images in Figure 3 demonstrate the effect of the DMF wash. Figure 3(a) shows two images of CNTs filled with 5wt% PAN solution prior to the DMF wash. Before the wash, a large amount of PAN can be seen clinging to the outer surface of the CNTs. To clear up the outer PAN so that the structure of PAN inside the CNTs becomes more apparent, the sample was rinsed in DMF for 1 hour at 80°C. Figure 3(b) shows two images of the sample after the DMF rinse. There is still some polymer clinging to the outer walls of the CNTs, but the amount of PAN on the outer walls is significantly less. As a result, the PAN structure within the CNTs becomes much more apparent.

The webbing underneath the CNTs is the lacey carbon

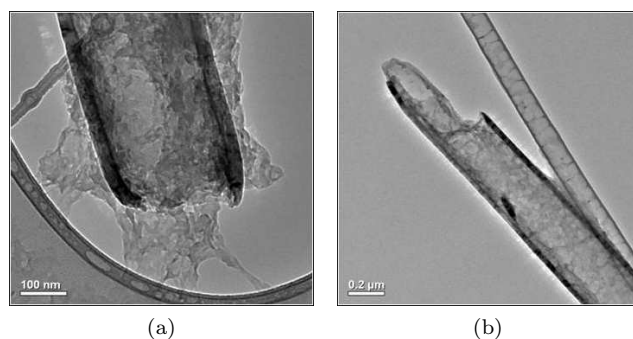


FIG. 3: TEM images of before and after DMF rinsing. Samples are filled with 5wt% PAN/DMF solution. (a) Before DMF rinsing. (b) After 1 hour DMF rinse at 80 °C.

supporting the CNTs on the TEM grid. The density of CNTs on the TEM grid was much less after the rinse because some of the CNTs were probably washed off the grid by the DMF. Longer or higher temperature DMF rinse is expected to entirely clear up the PAN clinging to the outer wall of the CNTs, and eventually also dissolve away the PAN inside the CNTs.

Extent of polymer filling

To quantify the extent of PAN filling in the CNTs, there are three main parameters in the whole process that can be altered: the concentration of the PAN solution, the time period of DMF rinsing, and the temperature of the DMF rinse. Each of these parameters is discussed below.

The TEM images in Figure 4 show CNTs filled with PAN of different concentrations. These images were taken after the samples were rinsed in DMF for 1 hour at 80°C. The images show that the CNTs are completely filled by PAN for all five concentrations. All five samples exhibit the rough, solid pockmarked structure that was also shown in Figure 3. These results indicate that the filling of the CNT is not affected by the concentration of the PAN/DMF solution. This makes sense because in the diffusion process used to fill the CNTs, the solvent of the solution (DMF) is constantly evaporating, causing the concentration of the solution to be enriched. A diagram of this process is shown in Figure 5.

In the process depicted in Figure 5, the diffusion of PAN into the CNTs is very quick, and the concentration inside and outside the CNTs equilibrate within seconds after the PAN solution has been deployed onto CNTs. However, as time passes, the solvent of the PAN solution begins to evaporate and the PAN concentration in solution becomes enriched. As a result, a new concentration gradient between the inside and outside of the CNTs is created and the CNTs are continually filled until it is completely full with PAN. Since the PAN concentration is constantly enriched because of evaporation of DMF,

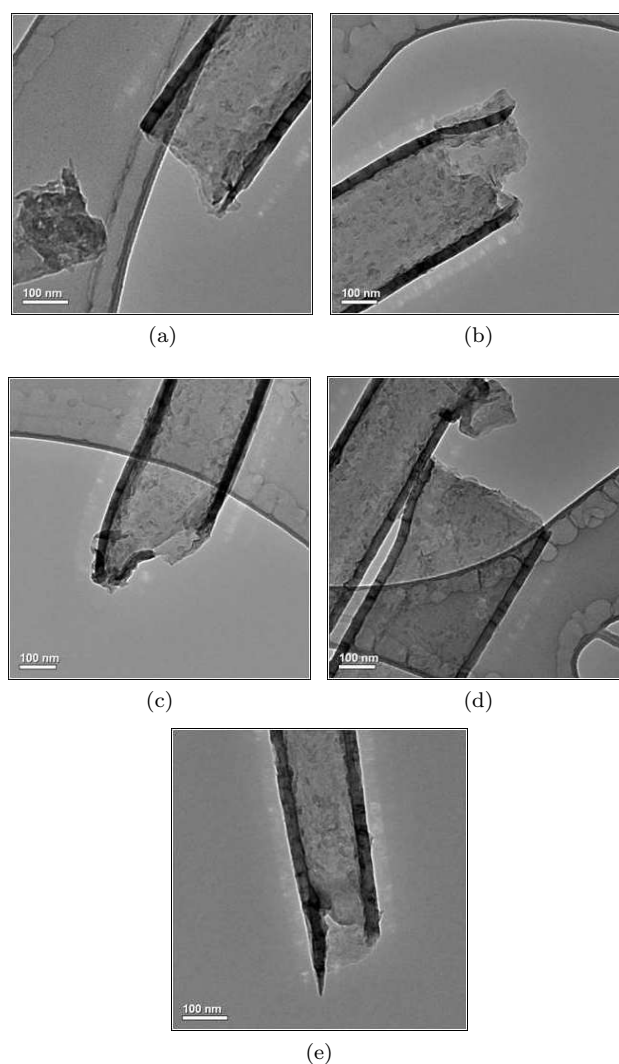


FIG. 4: TEM images of CNTs filled with different concentrations of PAN/DMF solution. Images were taken after DMF rinse for 1 hour at 80 °C. (a) 0.1wt% solution. (b) 0.5wt% solution. (c) 1wt% solution. (d) 2wt% solution. (e) 5 wt% solution.

the initial concentration of the PAN/DMF solution does not affect the filling of the CNTs.

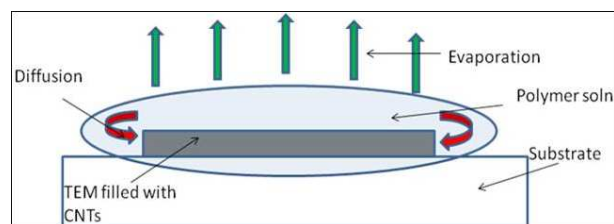


FIG. 5: Diagram demonstrating how CNTs are filled with PAN.

The two TEM images in Figure 6 show two 0.5wt%

PAN solution filled CNTs samples that have been rinsed in DMF for different times. Figure 6(a) shows a sample that has been rinsed for 2 hours at 80°C and Figure 6(b) shows a sample that has been rinsed for 21 hours at 80°C. Although the two samples were rinsed for very different times, the PAN structure shown in the images are almost identical. Figure 6 demonstrates that the time of rinsing only affects the outside of the CNTs and not the inside of the CNTs.

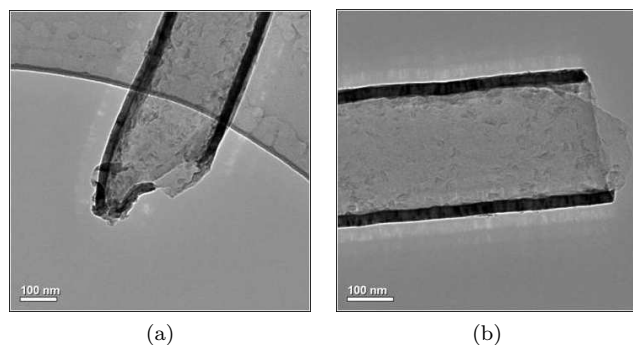


FIG. 6: DMF rinsing for two different time periods of 0.5wt% PAN solution filled CNTs. (a) DMF rinsed for 2 hours at 80 °C. (b) DMF rinsed for 21 hours at 80 °C.

Intuitively, it is expected that the PAN inside the DMF should also be dissolved. The images may indicate extremely long diffusion times (greater than 21 hours), or some unknown mechanism that is preventing the PAN to dissolve. The effect of DMF on the PAN inside the CNTs needs to be studied more thoroughly to explain the unusual behavior between PAN and DMF. So far, DMF rinse has been only tested at two temperatures: 60°C and 80°C. The resulting PAN structure inside the CNTs is almost identical indicating that temperature has an insignificant affect on the rate at which PAN dissolves in DMF. The upper limit of rinsing temperature was kept at 80°C to prevent any possibility of thermal degradation of the polymer. The range of temperatures used here does not seem to influence the PAN structure inside the CNTs.

Carbonization

The TEM images in figure 7 show PAN filled CNTs before and after the carbonization process. Carefully analysis between Figure 7(a) (before carbonization) and Figure 7(b) (after carbonization) suggest that the PAN structure within the CNTs after the carbonization is more opened and less packed. This may indicate a porous structure. However, more trials of this experiment need to be performed to ensure repeatability of this finding.

Notice the CNT walls after the carbonization are thinner and look to be damaged. CNTs do not begin to deteriorate until temperatures well above 750°C. Therefore, either these CNTs contain a lot of impurities, or

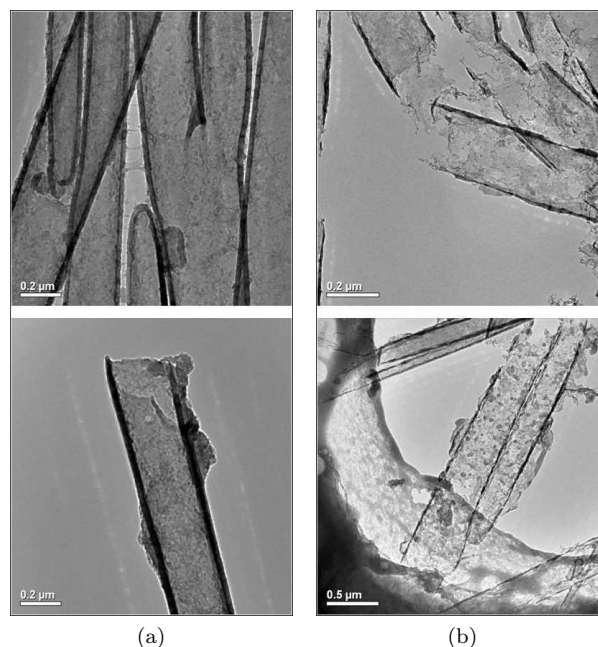


FIG. 7: TEM images of PAN filled CNTs before and after carbonization process. (a) Before carbonization. (b) After carbonization.

impurities from the PAN are eating at the CNTs. This issue needs to be addressed in the future.

Conclusion

This study has demonstrated that using the same technique as that shown in Bazilevsky *et al.*¹, CVD CNTs can be filled with PAN, a carbonizable polymer. Multiple experimental runs of the intercalation process with PAN demonstrate that the PAN structure inside CNTs does not resemble the peapod, foam, or bubble structure described in Bazilevsky *et al.*¹

Furthermore, experimental results indicate that the extent of polymer filling is insensitive to the concentration of the initial polymer solution and the time period that a sample is rinsed in the DMF. This makes sense because the diffusion process used for the intercalation of CNTs constantly enriches the PAN solution around the CNTs maintaining a concentration gradient. However, the ineffectiveness of the DMF washing time is very counterintuitive because it is expected that given a long enough time period, the PAN inside the CNTs should also be dissolved by the solvent. The results from the DMF washing time experiment suggests that either the diffusion time of DMF into the CNTs is beyond 21 hours, or some unknown mechanism or process is taking place that prevents the DMF from solvating the PAN in the CNTs. Temperature effects have not yet been thoroughly studied and so far no change can be detected between a wash at 60°C and a wash at 80°C.

Finally, one experimental run of the carbonization step has been performed. The results that were obtained show some damage to the CNT walls. The PAN structure within the CNTs does indicate some differences between the filled CNTs samples before and after the carbonization process. However, a method for carbonization of PAN filled CNTs has been developed, and further studies can be performed to improve the morphology of PAN intercalated in CNTs for nano-filter applications.

Acknowledgements

The financial support of the Department of Defense and the National Science Foundation under Grant NSF EEC 0453432.

-
- ¹ A. V. Bazilevsky, K. X. Sun, A. L. Yarin, and C. M. Megaridis, *Langmuir* **23**, 7451 (2007).
 - ² J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, *Carbon* **44**, 1624 (2006).
 - ³ T. M. Squires and S. R. Quake, *Reviews Of Modern Physics* **77**, 977 (2005).
 - ⁴ P. A. Thompson and S. M. Troian, *Nature* **389**, 360 (1997).
 - ⁵ A. L. Yarin, A. G. Yazicioglu, C. M. Megaridis, M. P. Rossi, and Y. Gogotsi, *Journal Of Applied Physics* **97** (2005).
 - ⁶ Z. M. Liu, X. H. Dai, J. Xu, B. X. Han, J. L. Zhang, Y. Wang, Y. Huang, and G. Y. Yang, *Carbon* **42**, 458 (2004).
 - ⁷ T. Kyotani, T. Nagai, S. Inoue, and A. Tomita, *Chemistry Of Materials* **9**, 609 (1997).