Polyimide/Carbon Nanocomposites

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Synopsis of Project

The goal of this product is to design and characterize well-defined conductive nanocomposite materials. The materials will be composed of a polymer matrix composed of rigid-backbone polyimides, and will be filled with modified or unmodified multi-walled carbon nanotubes (MWNTs). The ultimate design of this project is to create composite materials with optical clarity and a high conductivity.

Introduction

The use of chemical derivatization of both multiwalled and single walled carbon nanotubes has been known for some time, and has been shown to increase the solubility of the nanotubes in common organic solvents.

Following the results of the previous quarter, in which it was determined that functionalization of the MWNTs resulted in MWNTs with vastly increased solubility characteristics, attempts at direct formulation of nanocomposite materials was the next logical step. Such "first-generation" composite materials suffered from several problems, which included incomplete and unstable dispersions which quickly formed aggregates during the film casting process.

Following this, it was determined that long chain aliphatic amines such as hexyl-and octyl-amine vastly increase the solubility of MWNTs, to the point that even nonfunctionalized MWNTs can be made soluble in a 1% solution of octylamine in DMF. It is believed that such amines act as surfactants for the MWNTs, effectively preventing aggregation which leads to meso- and microscale domain separation in the composite materials.

Improvement upon the existing methodology for carboxylation of MWNTs was needed, due to the fact that refluxing in 5.0 M HNO_3 for 2 hours has shown to be not very effective for breaking up large-scale entangled aggregates of nanotubes. In such cases, the MWNTs on the outside of the aggregates get functionalized while the inner nanotubes are believed to remain pristine. The result is that highly aggregated MWNT samples show extremely low solubility post amine functionalization compared with MWNT samples with lower aggregate content. It is known that nitric acid exfoliates SWNT bundles, and that sonication also plays a significant role in the disruption of bundles and aggregates. Towards these ends, a new, high-yield method employing sonication of the nanotubes in concentrated nitric acid was employed.

The films cast are divided into two separate "generations". The first generation composites are those composites of MWNT, MWNT-COOH, and MWNT-ODA with poly (*bis*-ADA-DCB), using dry, distilled DMF as a solvent. The second generation systems used octylamine as a surfactant for the nanotubes, in the form of a 1% solution in DMF. Both the first and second generation films displayed undesirable characteristics such as inhomogeneous dispersion or lack of conductivity.

To cope with the shortcomings, two alternate approaches were tried. The first employed carbon nanocapsules, similar to carbon nanotubes in structure with the exception of having closed tube ends. It is expected that the average size of the nanocapsules will be smaller than that of the MWNTs; as a result, there are expected to be far fewer agglomerate structures.

The second approach was to bind the DCB (2,2'-dichloro-4,4'-diaminobiphenyl) monomer to the carboxylated nanotubes in the same manner as that employed for the synthesis of the ODA functionalized tubes. The MWNT-DCB modified tubes could then be co-polymerized with DCB and *bis*-ADA to grow polymer chains off the surface of the nanotubes. Such polymer-modified

nanotubes are expected to have tremendously improved compatibility and dispersion in the poly-(*bis*-ADA-DCB) polymer matrix.

Experimental

I. Synthesis

A. Improved Synthesis of Carboxylated MWNTs

656.9 mg of pristine MWNTs obtained from Prof. Liming Dai (U. Akron) were subjected to sonication in 5 mL concentrated nitric acid at 25 °C for one hour. Following this, the sample was filtered over a 0.45μ polypropylene filter and washed once with 50 mL of distilled water, then 4 times with 50 mL of isopropanol. The sample was then collected and dried under vacuum (30 in Hg) for 24 hours at 70 °C. Yield: 637.6 mg (97%). Degree of functionalization was estimated by thermogravimetric analysis on a TA instruments TGA to be 1.30% by weight.

B. Carboxylation of Carbon Nanocapsules (CN-COOH)

121.2 mg of carbon nanocapsules were suspended in 15 M HNO_3 and sonicated at 25 °C for 1 hour. Following the sonication, the sample was filtered over a 0.45μ polypropylene filter and washed once with 50 mL of distilled water, followed by 4 additional washings with 50 mL of isopropanol. The sample was then collected and dried under vacuum (30 in Hg) for 24 hours at 70 °C. Yield: 61.1 mg (50.4%).

C. Modified Amine Functionalization of MWNT-COOHs: MWNT-ODA.

433.1 mg of MWNT-COOHs prepared as described above were heated in 4.4767 grams of octadecylamine melt at 120 °C for 8 days. The mixture was then cooled and sonicated in 20 mL 1:1 isopropanol:THF for 1 hour. The resulting solution was filtered over a 0.45μ polypropylene

filter and then washed 3 times with 50 mL of THF, followed by 2 additional washings of 50 mL isopropanol. The sample was then collected and dried under vacuum (30 in Hg) for 48 hours at 90 °C. Yield: 417.8 mg (96%). Overall yield from pristine MWNTs to MWNT-ODA: 93%. The degree of functionalization was measured by thermogravimetric analysis, and found to be 7.60%.

D. Monomer Functionalization of MWNT-COOH: MWNT-DCB

68.4 mg of MWNT-COOHs were weighed into a glass vial and stirred in 1.4227 grams of DCB melt at 180 °C for 8 days. The mixture was then cooled and sonicated in 20 mL 1:1 isopropanol:THF for 1 hour. The resulting solution was filtered over a 0.45μ polypropylene filter and then washed 3 times with 50 mL of THF, followed by 2 additional washings of 50 mL isopropanol. The sample was then collected and dried under vacuum (30 in Hg) for 48 hours at 90 °C. Yield: 61.6 mg (90%). Overall yield from pristine MWNTs to MWNT-ODA: 87%. The degree of functionalization was measured by thermogravimetric analysis, and found to be 4.05%.

E. Synthesis of poly-(bis-ADA-DCB) Functionalized MWNTs

13.2 mg of MWNT-DCBs were mixed with 237.2 mg of DCB in a three neck flask under N_2 and purged for several minutes. 10.00 mL of freshly distilled *m*-cresol was added to the flask and the reaction stirred with a mechanical stirrer with mild heating until all of the DCB had dissolved and the MWNT-DCBs were sufficiently dispersed in solution. The result was a black, viscous solution.

Following this, the reaction mixture was cooled to room temperature and 499.7 mg of *bis*-ADA was added to the flask. The mixture was allowed to stir at room temperature at a rate of 150 RPM for four hours, after which the temperature of the reaction was raised to 200 °C and

stirred overnight. The reaction was then cooled, and precipitated in methanol to form long grayish fibers.

The fibers were collected, allowed to dry slightly, and then dissolved in a mixture of 1:1 hot DMF:cresol. This mixture was then filtered over a 0.45μ polypropylene filter to remove any homopolymer from the product. Following the removal of the main bulk of homopolymer, the sample was washed with one 250 mL fraction of DMF, followed by three 250 mL fractions of THF, with a final rinse of three 50 mL fractions of isopropanol. The product was then weighed and dried at 70 °C under vacuum overnight. Final mass of the product: 11.9 mg. Final analysis of the results of this reaction are currently underway. Analysis by TGA and AFM are planned in order to fully characterize the sample, and results of initial ATR FT-IR studies are still being analyzed. It is expected that molecular weight characterization by GPC will prove impossible, due to the relative size of the nanotubes; as a result light scattering will be investigated as an alternative.

It should be noted that in order for this procedure to have any industrial applicability, two shortcomings must be addressed: First, the monomer derivatization of the nanotubes is extremely slow-the time necessary to achieve high conversion of the carboxyl groups being necessarily greater than the eight days observed to give a 40% conversion. Second, the post-polymerization filtration step is very slow. Correcting this would require that the solution be extremely dilute.

II. Analytical Results

A. Thermogravimetric Analysis (TGA)

In order to ascertain the extent of functionalization on the nanotubes following carboxylation and derivatization with octadecylamine, a TA Instruments TGA-2950 thermogravimetric analyzer was used. For the pristine MWNT and carboxylated MWNT samples,

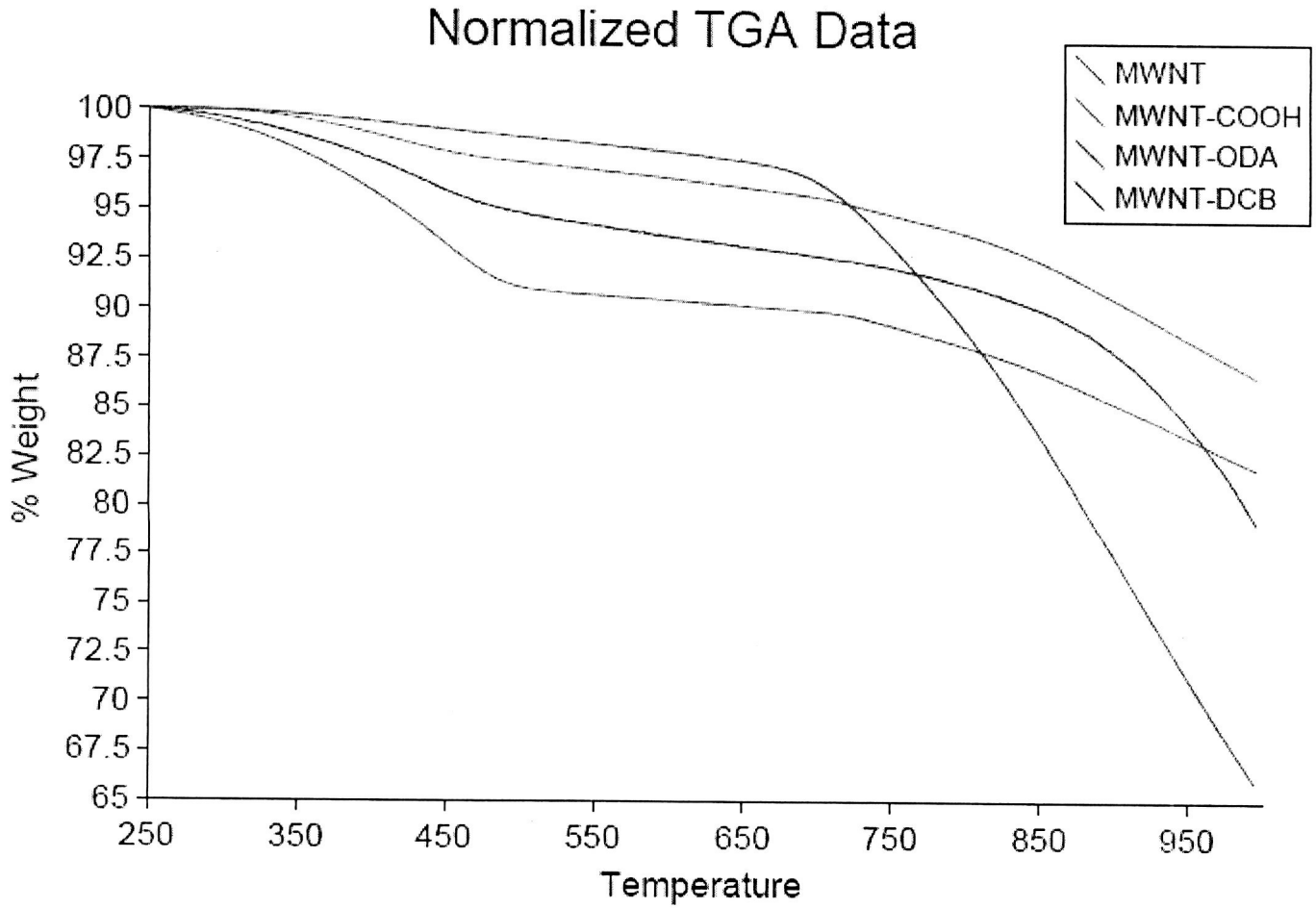
the samples were maintained at a constant temperature of 250°C under a nitrogen atmosphere for two hours before ramping at 10 °C / min up to a maximum temperature of 1000 °C. For the CN, CN-COOH, MWNT-ODA and MWNT-DCB samples, they were held at a constant 100 °C for two hours, then ramped at 10 °C / min up to 1000 °C. These samples were held at a lower temperature to insure that there was no early loss of substituent, as the decomposition temperature was not known.

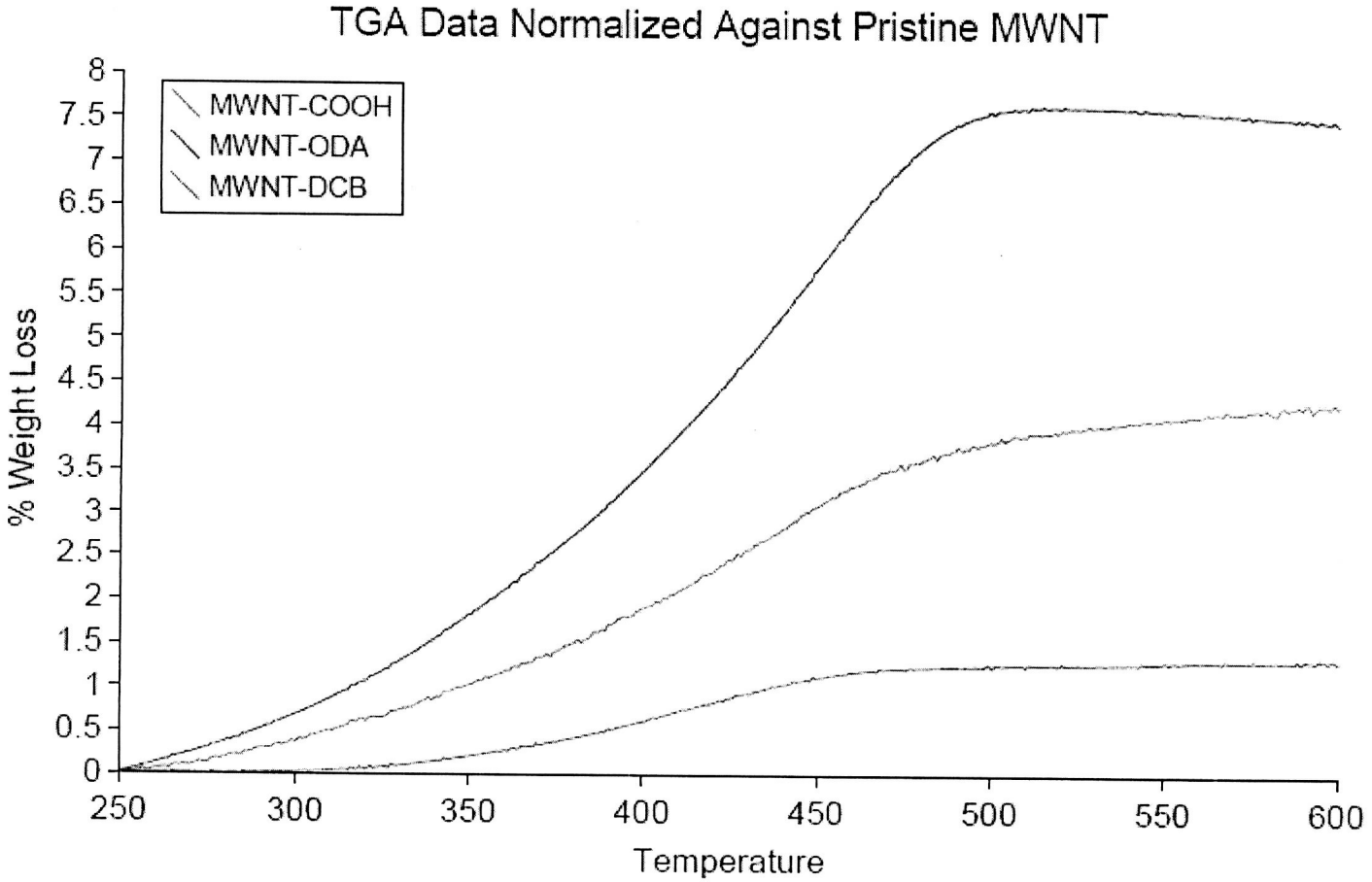
The first plot shows the results for the three samples run, normalized against the pristine MWNT sample. The graph ranges from 250 °C to 1000 °C, because even in the case of the ODA and DCB samples, which were held constant at 100 °C, there are no significant changes to speak of. Starting at ~300 °C, loss of the carboxyl groups is observed, though the process in the DCB and ODA functionalized tubes starts at ~250 °C. At ~500 °C, all of the functional groups have been removed and the nanotubes have reverted to a pristine state. Continued heating above 650 °C results in the decomposition of the nanotubes. The most likely mode of decomposition is that of the outer layers being stripped off one by one; such a process is catalyzed by the presence of any residual metal particles – usually only a concern in the pristine nanotube samples. It is known that SWNTs are stable up to and above 1000 °C.

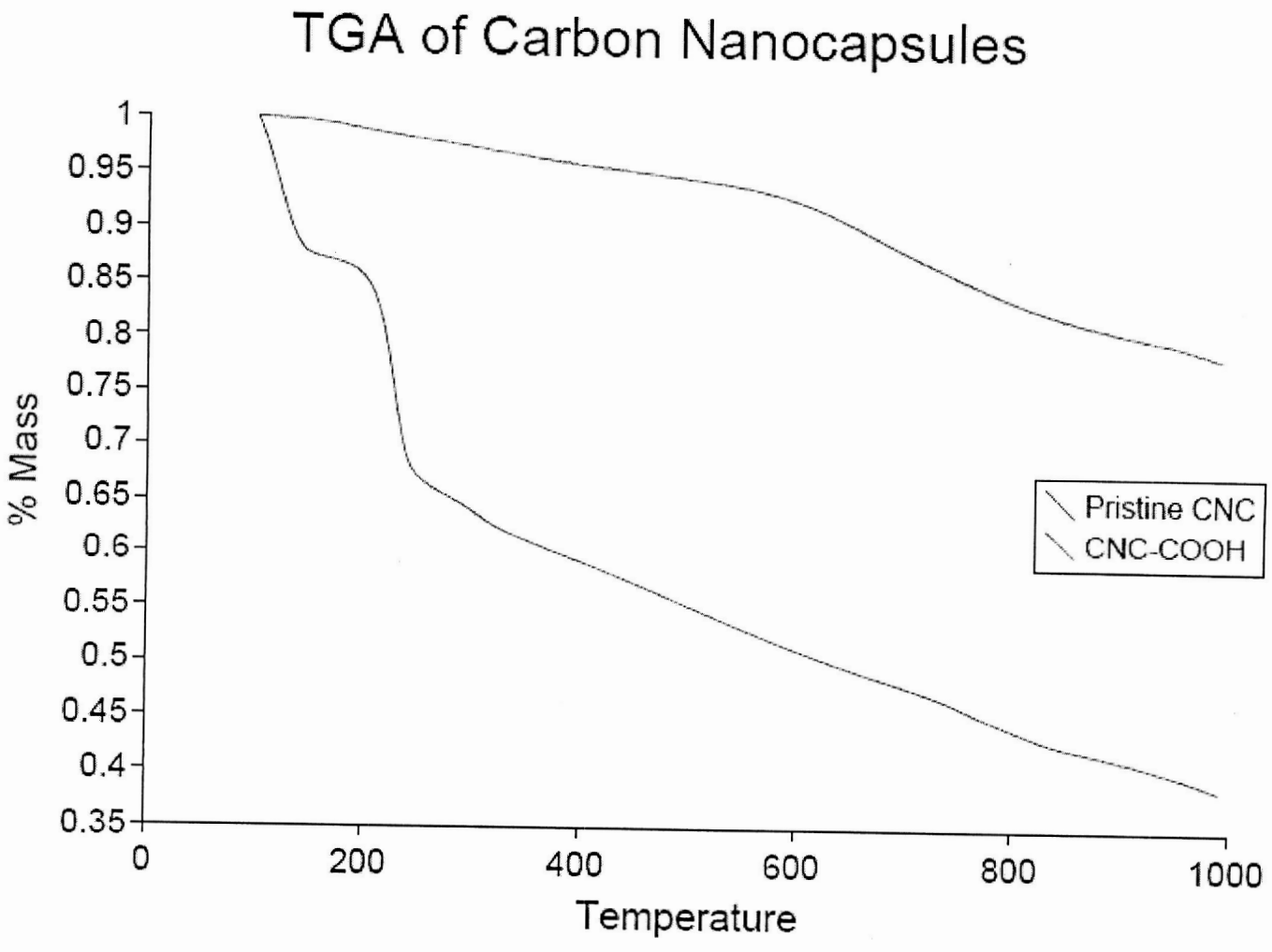
There is a marked difference in the rate of decomposition of the pristine MWNTs as compared to that of the functionalized MWNTs. It has been shown that residual iron or cobalt from the initial synthesis of the nanotubes catalyzes the decomposition of the nanotubes. This conclusion is reinforced by the much slower decomposition of the modified MWNTs, which have been treated with acid during the initial carboxylation step. Any residual metals would be removed during this process.

In the second plot, the pristine MWNT TGA plot is used as a baseline and subtracted from the other two sets of sample data. From the graphs, it is becomes trivial to ascertain the extent of functionalization in the samples. In the case of the carboxylated MWNTs, 1.30% of the total mass is due to COOH groups. When the carboxylated tubes are functionalized with octadecylamine, it is observed that 7.60% of the total sample mass is due to the [$COO^{-}NH_2(CH_2)_{17}CH_3$] groups, which leads to the conclusion that approximately 83% of the available carboxyl groups have been successfully converted. The TGA of the DCB functionalized nanotubes indicates approximately 4.05% functionalization, indicating that only 40% of the available carboxyl groups have been successfully functionalized. Although the exact reason for the lower degree of functionalization is unknown, extending the reaction time from eight days to sixteen days should significantly increase the extent of functionalization.

The third plot shows the results of thermogravimetric analysis for the as-received and carboxylated carbon nanocapsules (CNCs). From the graph, it is obvious that there is an impurity present in the nanocapsules, most likely that of an organic small molecule, possibly ferrocene – a commonly used precursor to carbon nanotube and nanocapsule formation. Strangely, the carbon nanocapsules as received also displayed marked solubility in water, something which no other sample has done, included the carboxylated nanocapsules. It is likely that the process of sonication in concentrated nitric acid oxidizes and removes any traces of impurities present in the nanocapsules, resulting in a cleaner sample. Due to the unexpected weight loss of the pristine CNC sample, it is impossible to accurately determine the extent of carboxylation in the subsequent oxidation reaction.


Normalized TGA Data
MWNT
MWNT-COOH
MWNT-ODA
MWNT-DCB
100
97.5
95
92.5
90
87.5
85
82.5
80
77.5
75
72.5
70
67.5
65
% Weight
250
350
450
550
650
750
850
950
Temperature


TGA Data Normalized Against Pristine MWNT
MWNT-COOH
MWNT-ODA
MWNT-DCB
% Weight Loss
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
250
300
350
400
450
500
550
600
Temperature


TGA of Carbon Nanocapsules
% Mass
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0
200
400
600
800
1000
Temperature
Pristine CNC
CNC-COOH

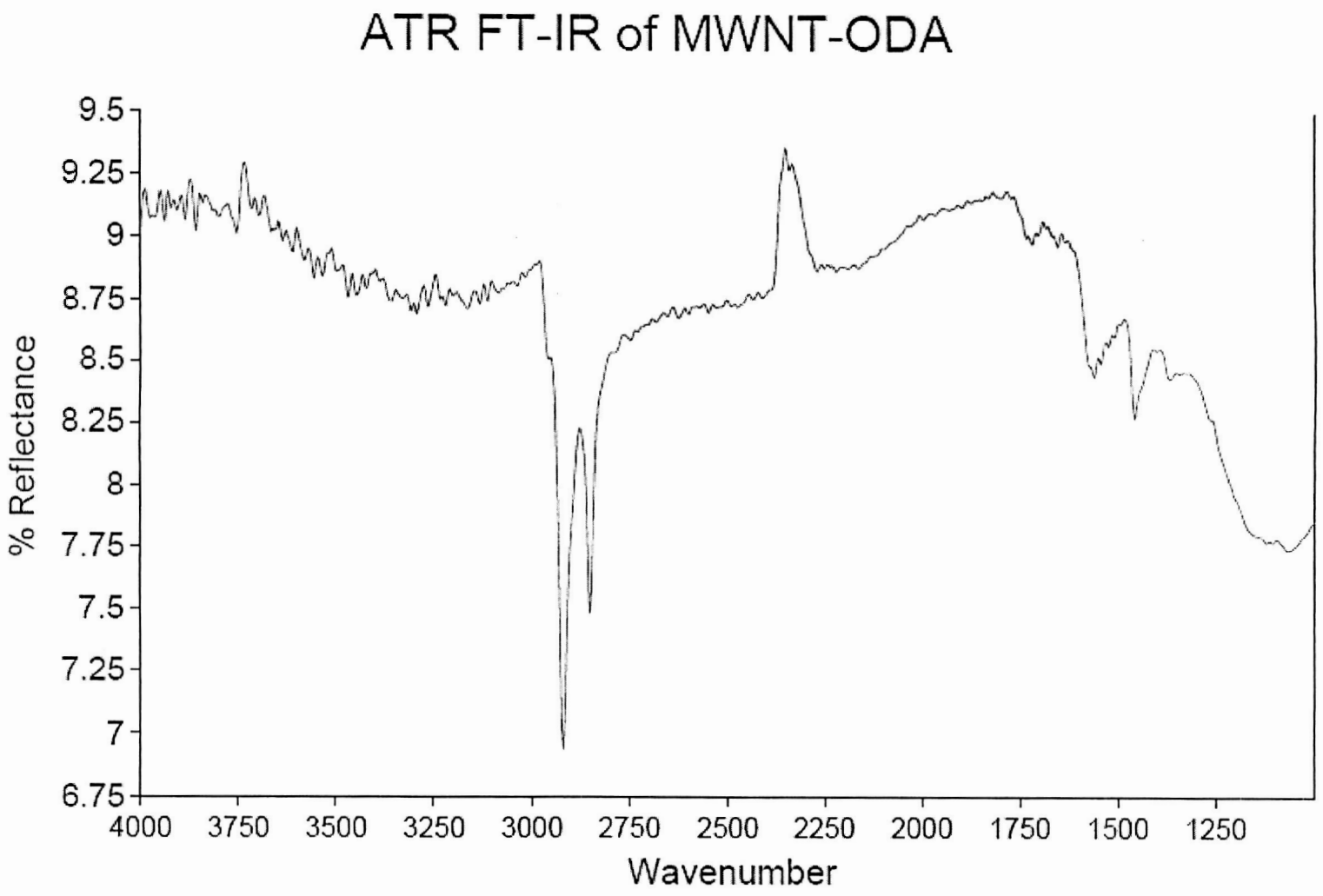
B. Attenuated Total Reflectance IR Spectroscopy

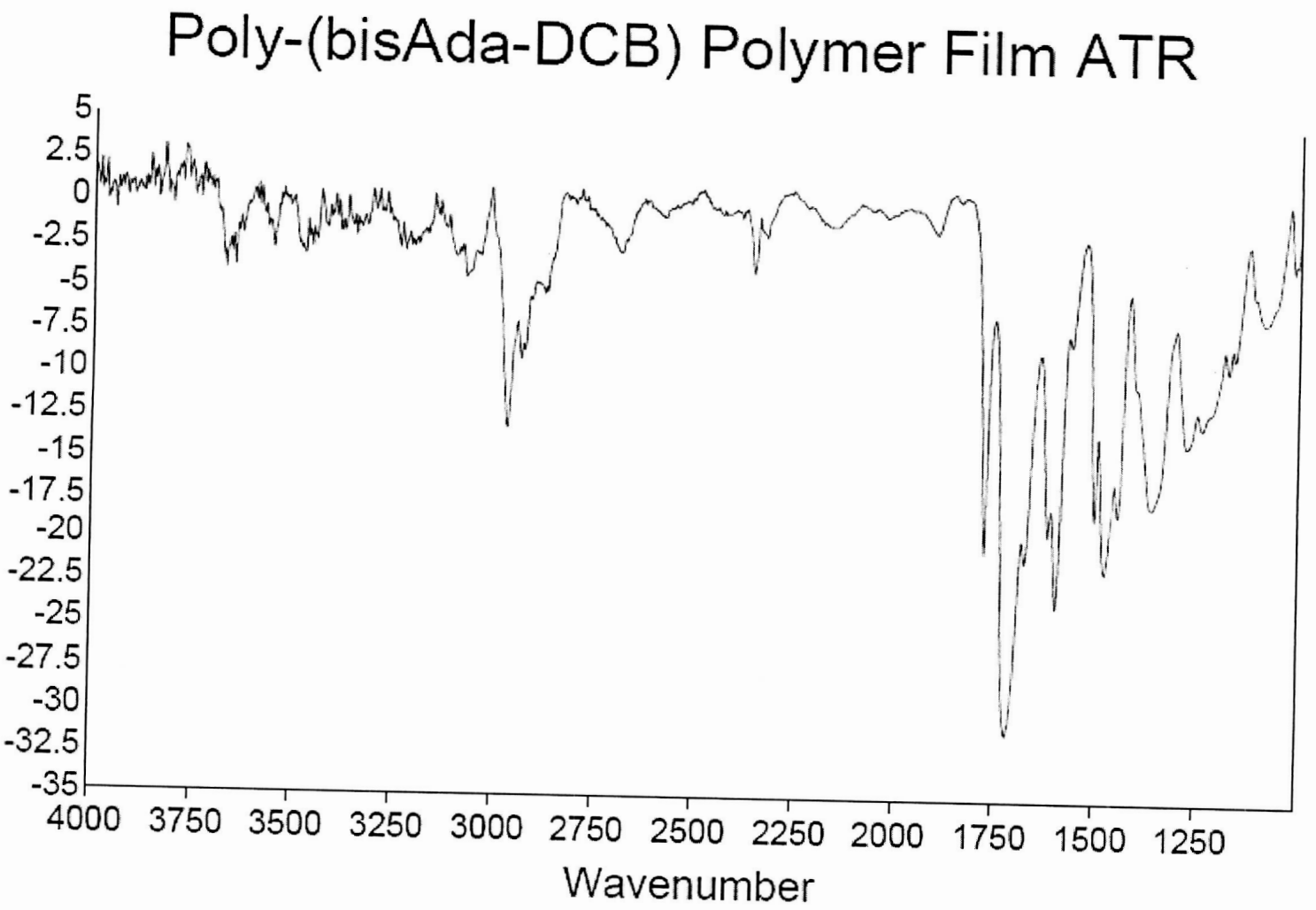
In order to characterize the functional groups present on the nanotube surface, IR spectra were gathered using an two mirror continuously variable ATR stage on a Digilab Excalibur series FT-IR, using a liquid nitrogen cooled low-temperature IR detector. Data was acquired with the detector aperture completely open and with a sensitivity setting of 8; the sampling rate was set to 5 KHz.

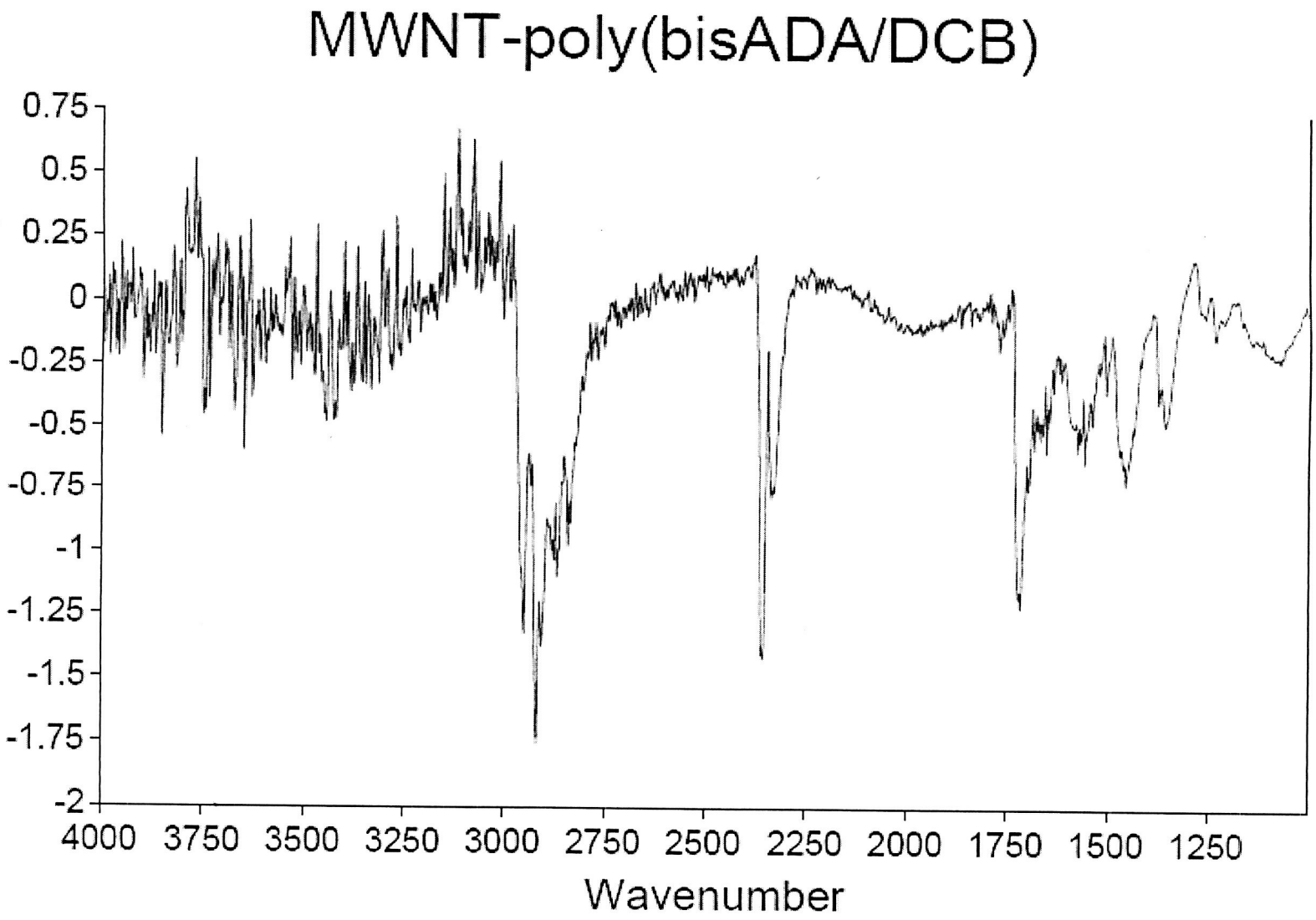
Although the pristine, MWNT-COOH, and MWNT-ODA samples were examined, only the MWNT-ODA sample displayed a spectrum which showed significant peak intensity. It is possible that in the pristine MWNT sample all of the modes of stretching present in the sample effectively cancel each other out due to symmetry. In the case of the carboxylated MWNT sample, since the carboxyl groups only compose 1.3% of the total sample weight, the effective concentration of IR active bond stretching (O-H and C=O) is too dilute to provide an adequate signal.

In the case of the MWNT-ODA sample, however, the ODA groups compose a higher relative mass of the sample. As a result, it was possible to see the presence of the octadecylamine groups. As shown in the spectrum below, C-H stretching from the eighteen methylene groups shows up as two strong bands, located at 2918 cm^{-1} and 2850 cm^{-1}. There is a faint, broad band at 1726 cm^{-1}, associated with the carbonyl group on the nanotubes. Additionally, there are two other significant bands, one at 1564 cm^{-1}, which is associated with NH scissor-type bending motions, and the second at 1462 cm^{-1}, which is due to CH_2 scissoring motions.

Additionally, results of ATR FTIR spectroscopy on poly-(*bis*-ADA/DCB) derivatized MWNTs has been performed, and the results compared with that of a pure polymer film. Assignments are still underway, but the results have been included for the sake of completeness.


ATR FT-IR of MWNT-ODA
% Reflectance
9.5
9.25
9
8.75
8.5
8.25
8
7.75
7.5
7.25
7
6.75
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
Wavenumber


Poly-(bisAda-DCB) Polymer Film ATR
5
2.5
0
-2.5
-5
-7.5
-10
-12.5
-15
-17.5
-20
-22.5
-25
-27.5
-30
-32.5
-35
4000 3750 3500 3250 3000 2750 2500 2250 2000 1750 1500 1250
Wavenumber


MWNT-poly(bisADA/DCB)
0.75
0.5
0.25
0
-0.25
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
4000 3750 3500 3250 3000 2750 2500 2250 2000 1750 1500 1250
Wavenumber

III. Film Casting

A. First Generation Films

The following procedure for preparing a 3.13% weight loading composite is detailed as a example for all first generation composite films. 60.7 milligrams of poly-(*bis*-ADA/DCB) and 1.9 mg of pristine MWNTs were placed in a vial. 2.00 milliliters of N,N'-dimethylformamide were added, and the vial securely sealed. The vial was vigorously shaken to dissolve all of the polymer, and then the mixture was then sonicated for 1 hour at 25 °C.

Following sonication, the sample was immediately pipetted onto a clean glass slide in a vacuum oven at 140 °C. The sample was then placed under a vacuum of 30 in Hg for 30 minutes to flash evaporate all solvent. The slide was then removed from the oven, allowed to cool, and the film removed from the slide with the aid of a razor blade. In almost all cases, the polymer film pulled away easily from the glass slide. The table below lists the samples created for the first generation of composites.

Generation 1

Sample Name	Type	MWNT, mg	Polymer, mg	DMF, mL	Loading	Quality
JTWI-27X5	ODA	1.9	60.7	2.00	3.1%	Inhomogeneous
JTWI-27 X6	ODA	3.9	63.7	2.00	6.1%	Inhomogeneous
JTWI-27 X7	ODA	7.4	62.3	2.00	11.9%	Inhomogeneous
JTWI-27 X8	ODA	1.3	132.6	2.00	1.0%	Inhomogeneous
JTWI-27 X9	COOH	1.4	60.0	2.00	2.3%	Inhomogeneous
JTWI-27 X10	COOH	6.1	58.7	2.00	10.4%	Inhomogeneous
JTWI-28 X11	COOH	3.0	59.2	2.00	5.1%	Inhomogeneous
JTWI-29 X12	COOH	1.2	136.3	2.00	0.9%	Inhomogeneous

B. Second Generation Films

For the second-generation composite films, a small percentage of an aliphatic amine was used as a surfactant for the nanotubes. Three different amines were used: butylamine, hexylamine, and octylamine. Of the three, hexylamine proved to have the best balance between solubility and

evaporation speed; octylamine exhibited detrimental polymer solubility issues at higher concentrations, and butyl amine evaporated too quickly, leading to poor dispersion in the final product.

The following table shows the various amines used, and the results for film casting experiments. It is important to note that a higher relative concentrations of the amine, the resulting polymer exhibits poor mechanical properties, and becomes a brittle film which flakes off the slide in small pieces. Only at concentrations of 1% and below is the amine concentration sufficiently low to allow good film formation as well as sufficient solubilization.

It is interesting to note the profound effect that the presence of an aliphatic amine has upon the solubility of MWNTs in solvents such as DMF. In the case of DMF, which is known to decompose into carbon monoxide and dimethylamine, it is important that all dimethylamine be removed from the DMF by vacuum distillation in order to get an accurate representation of the solubility of the MWNTs. Although it has not been tested, it is possible that dimethylamine contamination in DMF could lead to higher than expected MWNT solubility due to surfactant effects.

Generation 2

Sample Name	Type	Amine	MWNT, mg	Polymer, mg	DMF, mL	Amine, mL	% Amine	Loading	Quality
JTWI-30 7A	Pristine	Butyl	1.8	60.2	4.00	2.00	50%	3.0%	Brittle
JTWI-30 7B	COOH	Butyl	1.6	57.5	4.00	2.00	50%	2.8%	Brittle
JTWI-30 8A	Pristine	Butyl	2.1	60.6	1.33	0.66	50%	3.5%	Brittle
JTWI-30 8B	COOH	Butyl	2.3	59.8	1.33	0.66	50%	3.8%	Brittle
JTWI-30 9A	Pristine	Octyl	2.8	66.6	1.33	0.66	50%	4.2%	Brittle
JTWI-30 9B	COOH	Octyl	2.3	58.0	1.33	0.66	50%	4.0%	Brittle
JTWI-30 10A	Pristine	Octyl	0.8	124.8	2.66	1.33	50%	0.6%	Brittle
JTWI-30 10B	COOH	Octyl	0.7	116.0	2.66	1.33	50%	0.6%	Brittle
JTWI-30 11A	Pristine	Octyl	1.0	51.3	2.66	1.33	50%	1.9%	Brittle
JTWI-30 11B	COOH	Octyl	0.9	52.9	2.66	1.33	50%	1.7%	Brittle
JTWI-31 12A	Pristine	Octyl	1.0	57.8	1.80	0.20	11%	1.7%	Brittle
JTWI-31 12B	COOH	Octyl	1.1	57.6	1.80	0.20	11%	1.9%	Brittle
JTWI-31 13A	Pristine	Octyl	1.3	64.1	1.99	0.01	1%	2.0%	Good
JTWI-31 13B	COOH	Octyl	1.0	63.5	1.99	0.01	1%	1.6%	Good
JTWI-31 14A	Pristine	Octyl	1.7	61.5	1.99	0.01	1%	2.8%	Good
JTWI-31 14B	COOH	Octyl	1.7	63.4	1.99	0.01	1%	2.7%	Good
JTWI-31 15A	Pristine	Octyl	2.5	64.3	1.99	0.01	1%	3.9%	Good
JTWI-31 15B	COOH	Octyl	2.4	64.6	1.99	0.01	1%	3.7%	Good
JTWI-31 16A	Pristine	Octyl	4.6	60.1	1.99	0.01	1%	7.7%	Good
JTWI-31 16B	COOH	Octyl	0.6	65.4	1.99	0.01	1%	0.9%	Good
JTWI-31 17A	Pristine	Octyl	6.3	69.9	1.99	0.01	1%	9.0%	Good
JTWI-31 18A	Pristine	Octyl	9.9	62.5	1.99	0.01	1%	15.8%	Good
JTWI-34 16B2	COOH	Octyl	3.8	57.5	1.99	0.01	1%	6.6%	Good
JTWI-34 17B	COOH	Octyl	5.7	60.8	1.99	0.01	1%	9.4%	Good
JTWI-34 18B	COOH	Octyl	10.2	57.4	1.99	0.01	1%	17.8%	Good
JTWI-34 19A	ODA	Octyl	0.7	60.0	1.99	0.01	1%	1.2%	Inhomogeneous
JTWI-34 19B	ODA	Octyl	1.3	65.4	1.99	0.01	1%	2.0%	Inhomogeneous
JTWI-34 19C	ODA	Octyl	2.6	63.3	1.99	0.01	1%	4.1%	Inhomogeneous
JTWI-34 19D	ODA	Octyl	5.2	65.1	1.99	0.01	1%	8.0%	Inhomogeneous
JTWI-34 19E	ODA	Octyl	9.5	67.2	1.99	0.01	1%	14.1%	Inhomogeneous
JTWI-34 20	ODA	Octyl	0.8	64.9	1.99	0.01	1%	1.2%	Inhomogeneous
JTWI-34 21	ODA	Octyl	2.0	64.6	1.99	0.01	1%	3.1%	Inhomogeneous
JTWI-34 22	ODA	Octyl	3.0	63.4	1.99	0.01	1%	4.7%	Inhomogeneous
JTWI-34 23	ODA	Octyl	3.9	64.2	1.99	0.01	1%	6.1%	Inhomogeneous
JTWI-34 24	ODA	Octyl	5.9	64.6	1.99	0.01	1%	9.1%	Inhomogeneous

For the ODA modified MWNT composites, it was observed that micro-scale phase separation and aggregation occurred on a rapid scale in the presence of the aliphatic amine surfactant. It is believed that due to the high relative density of charges upon the surface of the MWNTs as a result of functionalization, the surfactant actually promotes phase separation. Such a situation would lead to the formation of micro-scale micelle-like aggregates. As a result, the second generation composites with ODA modified MWNTs were deemed unsuitable for further conductivity analysis. One possible method to limit the ionic character on the surface of the MWNTs would be to use a covalent attachment technique for the aliphatic amine, such as that reported by Chen *et. al* in which carboxylated MWNTs were treated with $SOCl_2$ prior to treatment with octadecylamine; however, such a procedure has the drawback of significantly reduced yield.

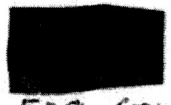
C. Appearance of the Films

For each film sample cast, a small portion of the film was cut and mounted on a clean piece of paper with transparent tape. The samples were then scanned using a CanoScan N650U scanner and processed using Adobe Photoshop. For all of the first generation films, the lack of adequate dispersion in the polymer matrix is plainly visible. The second generation films, on the other hand, display much better dispersion and homogeneity in all except a few cases – the samples with low nanotube loading (<2.0%) displayed almost ideal homogeneity.

1ST GENERATION

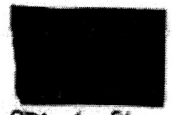
BLANK

0.88% COOH



5.0% COOH

0.98% ODA

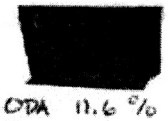


ODA 6.1%

2.3% COOH

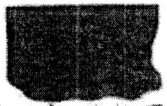
10.3% COOH

ODA 3.1%



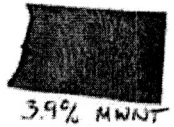
ODA 11.6%

2ND GENERATION

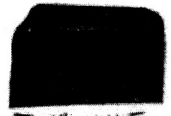


2.02% MWNT

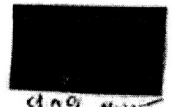
2.8% MWNT



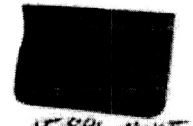
3.9% MWNT



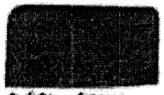
7.7% MWNT



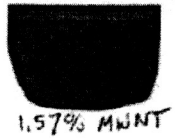
9.0% MWNT



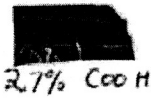
15.8% MWNT



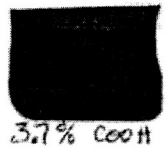
0.9% COOH



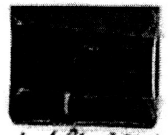
1.57% MWNT



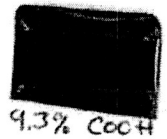
2.7% COOH



3.7% COOH



6.6% COOH



9.3% COOH

IV. Evaluation of Film Conductivity

The sample films were analyzed for conductivity by Prabhu Soundarrajan of Prof. Dai's group using a two probe technique. As shown below, in the case of the First Generation samples, the presence of micro-scale aggregates lead to inhomogeneous conductivity: the aggregates showed high conductivity offset by zones of pure polymer which displayed zero conductivity. As a result, in almost all cases, the associated error with the conductivity measurements equals or exceeds the value of the measurement itself. Such samples are deemed to be non-conductive, as they do not possess the homogeneous conductive qualities that are the goal of this project.

Loading	Generation	Agglomerates?	Conductivity (ohm*m)$^{-1}$	St. Dev	% Dev
			Pristine MWNT		
1.00%	1	Y	982	1,363	139%
4.00%	1	Y	2,673	2,595	97%
7.00%	1	Y	234	63	27%
10.00%	1	Y	405	512	126%
13.00%	1	Y	0	0	0%
			MWNT-COOH		
0.88%	1	Y	0	0	0%
2.30%	1	Y	0	0	0%
5.00%	1	Y	0	0	0%
10.30%	1	Y	0	0	0%
			MWNT-ODA		
0.98%	1	Y	0	0	0%
3.10%	1	Y	651,312	464,485	71%
6.10%	1	Y	8,988,504	9,471,253	105%
11.30%	1	Y	11,408,972	18,594,497	163%
11.60%	1	Y	1,013,884,573	481,159,757	47%

For the Second Generation composites the results were more consistent and promising. As shown in the table below, although all of the films possessed MWNT loadings comparable to those of the First Generation films, they were found to be consistently nonconductive. Although this would at first appear to be bad news, it is a good indication that the use of amine surfactants is indeed leading to homogenous dispersion of the MWNTs in the polymer matrix. It is believed that

the lack of conductivity is simply due to the loading content being below the percolation threshold for conductivity. In the case of the pristine MWNTs, some conductivity was observed for three samples; however, like the First Generation composites, the error of the measurement was so great that it is likely that some domain aggregation has still occurred within the samples, leading to localized zones of conductivity and insulation.

Pristine MWNT

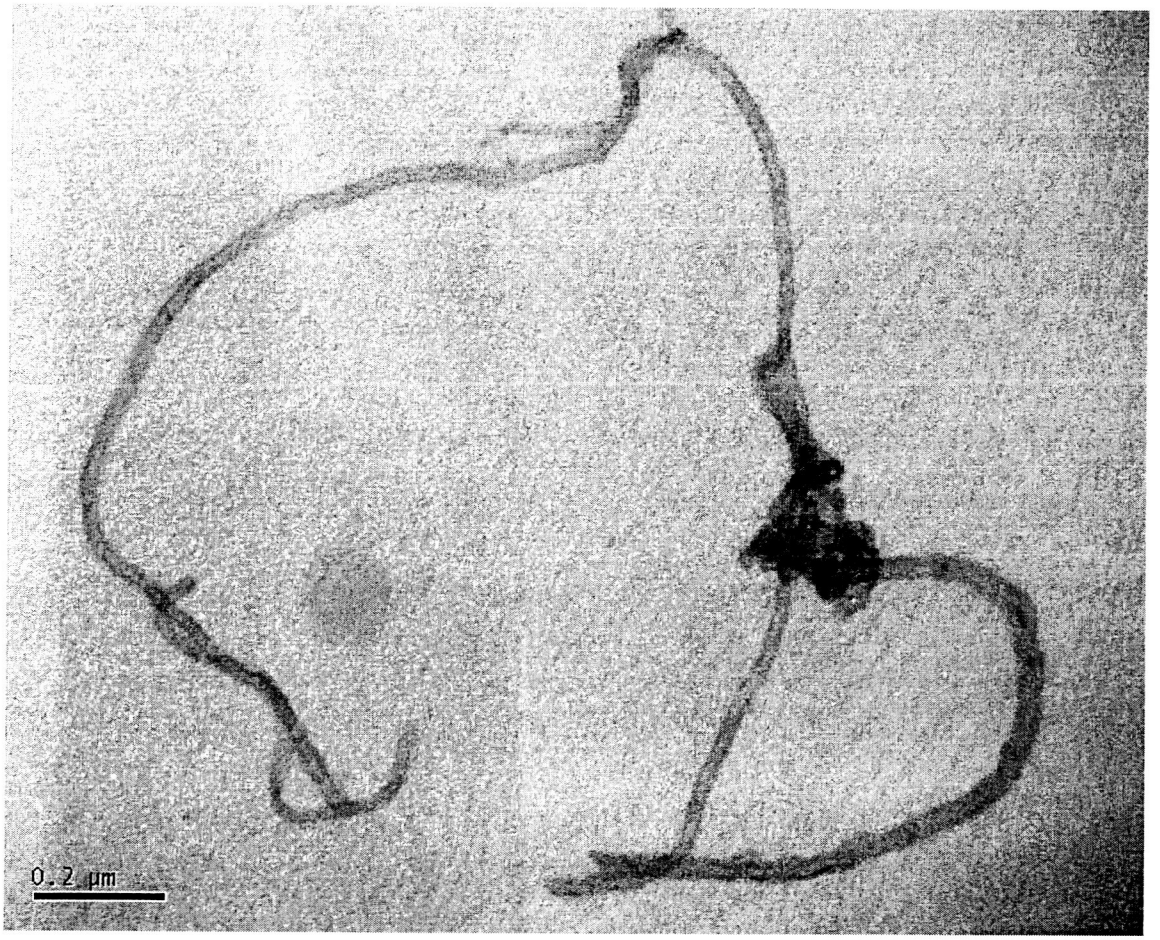
Loading	Generation	Agglomerates?	Conductivity $(ohm*m)^{-1}$	St. Dev	% Dev
2.02%	2	N	0	0	0%
2.80%	2	N	0	0	0%
3.90%	2	N	2,992,577	3,529,516	118%
7.70%	2	N	1,675,776	2,842,130	170%
9.00%	2	N	0	0	0%
15.80%	2	N	3,674,669	6,364,713	173%

MWNT-COOH

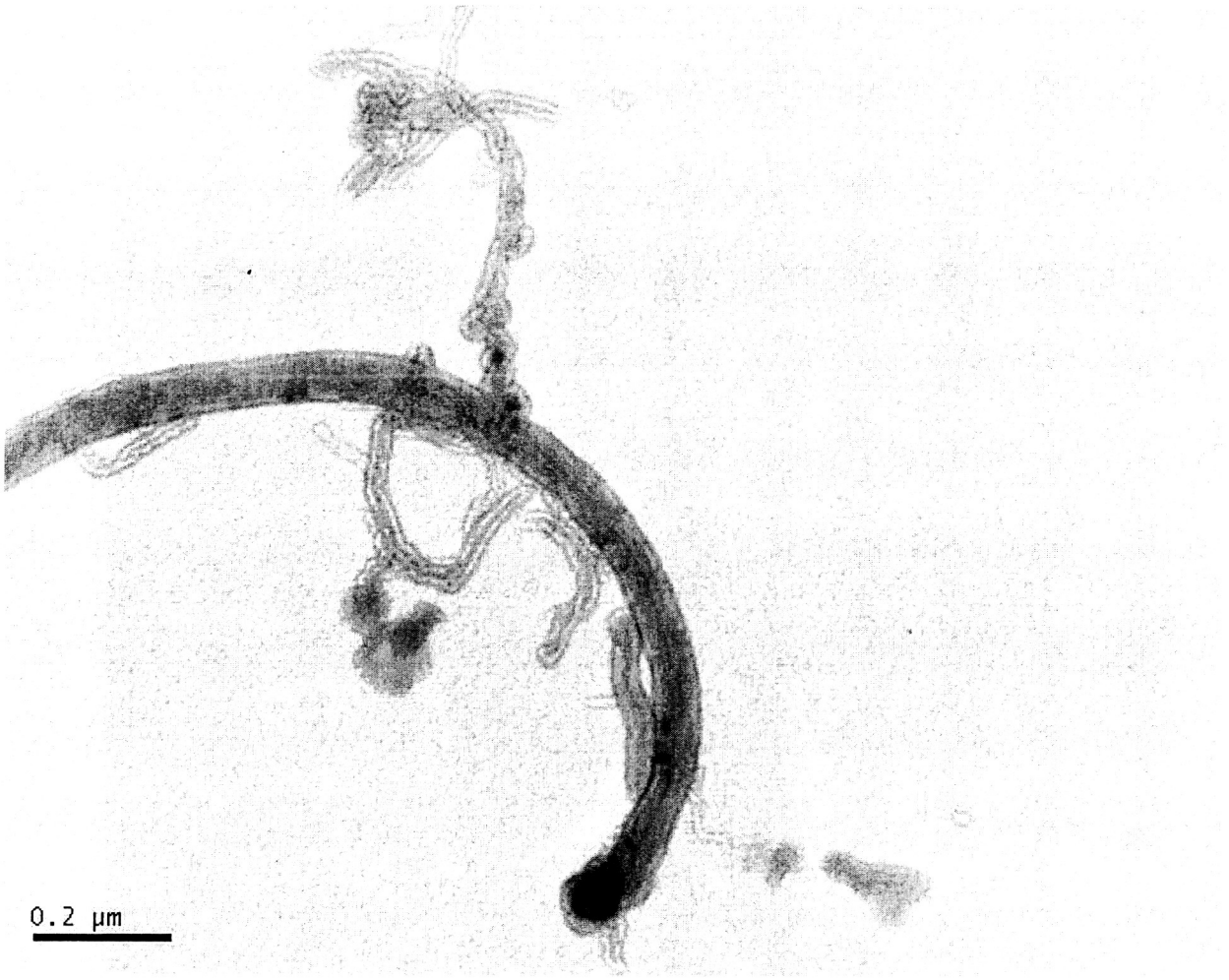
0.90%	2	N	0	0	0%
1.57%	2	N	0	0	0%
2.70%	2	N	0	0	0%
3.70%	2	N	0	0	0%
6.60%	2	N	0	0	0%
9.30%	2	N	0	0	0%
17.70%	2	N	0	0	0%

V. Transmission Electron Microscopy

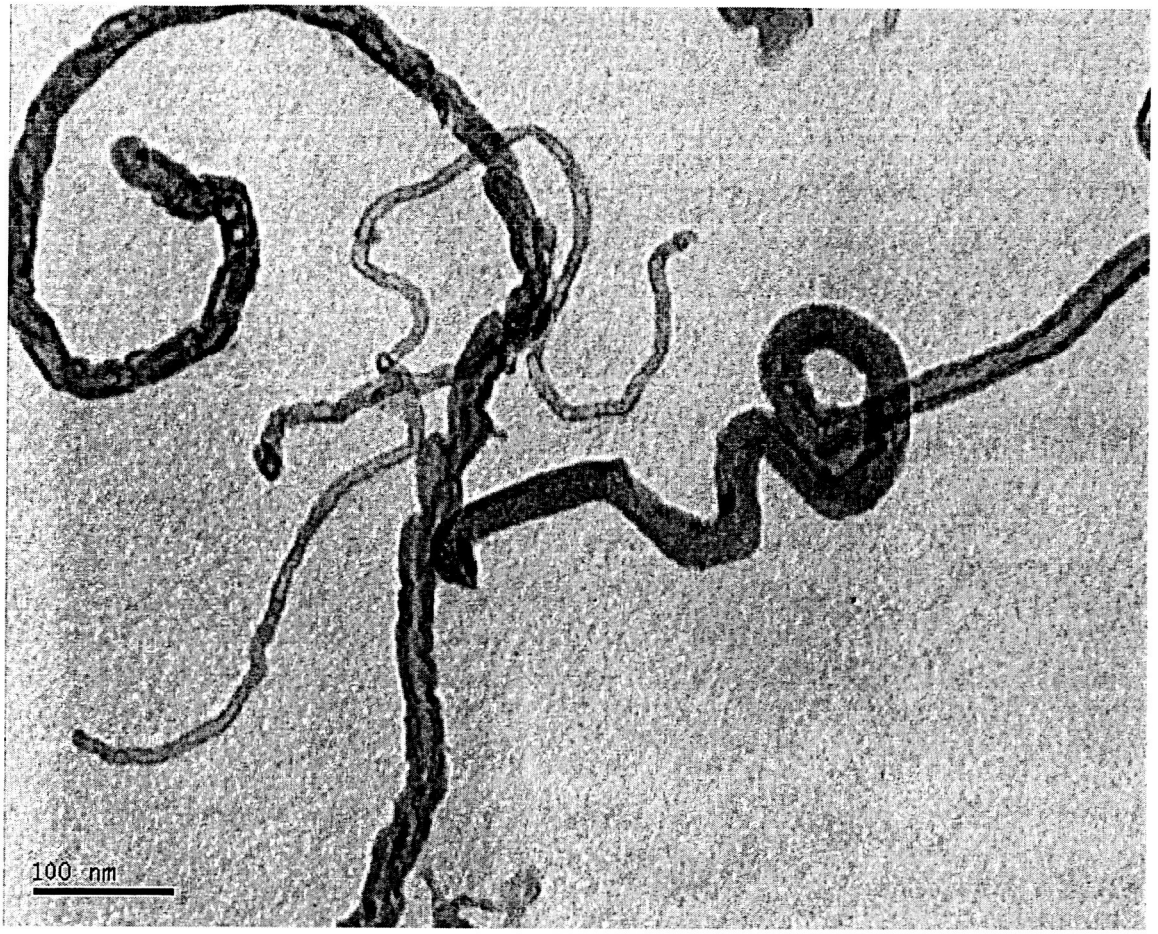
The nanotube samples were run on a Phillips STEM 1200 in TEM mode. The samples were dispersed in chloroform and transferred via pipette to carbon-coated nickel TEM grids for analysis. Below are shown representative images gathered for each of the samples. Below is a TEM image of the pristine nanotubes as received from Professor Dai. The vast majority of the nanotubes in the sample had diameters of ~50-100 nm, with lengths ranging from 500 nm up to 8 microns.



The following image is of a carboxylated nanotube sample made with the improved synthetic method. It is important to note that the harsh conditions of sonication in concentrated nitric acid did not result in any significant disruption of the overall tube structure. Additionally, large scale aggregates which were observed in the pristine nanotube sample, were reduced in number.



Finally, there is an image of the ODA functionalized nanotubes. The extended reaction in ODA melt for eight days did not result in any visible alteration of the nanotube structure. Similar to that observed for the carboxylated tubes, the number of nanotube bundles was markedly decreased from the original pristine sample, indicating that either the sonication, nitric acid, aliphatic amine, or a combination of the three, is working to disrupt the bundles.


100 nm